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► **To cite this version:**

Isabelle Billard. Green solvents in urban mining. *Current opinion in green and sustainable chemistry*, 2019, 2018-12-11, 18, pp.37-41. <10.1016/j.cogsc.2018.11.013>. <hal-02271235>

HAL Id: hal-02271235

<https://hal.science/hal-02271235v1>

Submitted on 26 Aug 2019

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Green solvents in urban mining

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Abstract. General considerations about urban mining and green solvents are first briefly discussed. Then, the use of green solvents in the recycling processes of technological objects present in urban mines is reviewed, focusing on metal recovery.

Keywords : urban mining, green chemistry, metal recovery, wastes

Scope

After promoting urban mining and defining green solvents, this paper, which is by no means exhaustive, reviews academic works. It is sorted by object types, chosen as iconic examples to highlight achievements and unresolved questions, because totally green processes are hardly found at the present stage. All the selected papers are dealing with real waste samples and the focus is on metal recycling [1] because the low plastic recovery rate of Waste Electrical and Electronic Equipment (WEEE) is detrimental to the overall recycling, while metal recovery is more efficient [2]. Whenever possible, a review describing current recycling methods has been mentioned.

Advocacy for concerned urban mining

The most obvious generic reason for harvesting compounds from anthropogenic wastes is the finite amount of matter on earth, especially metals, while the population increase and the desire of most humans to follow western consumption habits will unavoidably lead to scarce primary resources and abundant urban wastes.

Next, some specific reasons can be put forward. An immutable point is that pollution induced by direct landfilling (lead batteries, phosphor lamps with Hg etc.) is a time bomb. Then, volatile arguments are raw material prices, suffering sharp increases and decreases as exemplified by the rare earth (RE) crisis, difficulties in supply from unsafe countries, fear of monopoly and, last but not least, the quantity of raw materials to be found in urban wastes, which may be, but will not necessarily remain, higher than what can be found in natural ores [3]. Furthermore, most putrescible wastes are incinerated, thus providing energy in the form of heat. Although many plastics provide a calorific power similar to the oil which was used to synthesize them, one should not forget that thermic plant efficiencies are in the range of 30 – 40 %, and that burning plastic also means burning the brainpower involved in their design [4].

Therefore, as long as our preferred consumption mode will be “brand new and wonderful”, elemental recycling will be needed because the time lag between market launching and end of life makes the composition of to-be-recycled objects different from those under production. Recycling has to be done with great concern, as low range recycling in poor countries and the pollution induced to nature and humans is morally unacceptable [5].

What is a green solvent?

Until very recently, extraction and separation of metals from ores or technological objects were mainly based on a lixiviation step by use of mineral acids, followed by several steps of liquid-liquid extraction and/or selective precipitation. Thus, sophisticated extracting agents were the Holy

Grail of academic research, while diluent design was somewhat neglected. Following the (re)discovery of ionic liquids (IL) and Deep Eutectic solvents (DES), chemical formulation of solvents (re)appeared in the chemist agenda. Consequently, one could expect the academic world to conceive efficient green solvents, i.e. based on green chemistry principles and definition [6,7]. Unfortunately, in a provocative paper which sounds like a deserved smack, Jessop showed that this is more a dream than a reality [8]. Based on industrial initiatives, lists of green solvents have been published [8,9] but they remain limited. Ideas to address this problem are proposed in [8]. Life Cycle Analysis (LCA) from cradle to gate, thus determining the environmental impacts along industrial use, is necessary to assess green performances of any solvent [10,11]. A linear scale is however hard to establish so 2D diagrams are often presented [8,10] which render the choice between two solvents somewhat difficult. These methods could well apply to DES and ILs, provided that data on mass production are available, which is not yet the case [10]. Moreover, such studies are mainly focused on ILs for catalysis or organic synthesis for the fine chemical industry, which produces less wastes (in volume) than other chemical sectors [9,12]. Note that the greenness of mineral acids, mostly used for leaching of solid starting materials, has not yet been quantified, unless for methanesulfonic acid [13]. Families of green solvents are briefly discussed below.

Most traditional molecular organic solvents are not green. Once those miscible with water are discarded, the possible list for liquid/liquid extraction is rather limited [8,9].

LCA methods for ILs are hard to implement [14] because of several unknowns but it is clear that their synthesis protocols are not green and ILs are, most of the time, harmful to the environment [15]. ILs non-flammability and non-volatility are not enough to stamp them as green solvents. Some LCA papers compare ILs to organic solvents such as benzene, acetone, water [16] or toluene [17]. Results show that ILs shift environmental impacts towards their synthesis [12,16,17], while direct release of ILs during their industrial usage appears negligible. Therefore, efforts should be put on the recyclability of ILs [12]. Fortunately, greener ways to synthesize ILs do exist [17]. Potential improvement of ILs ecotoxicity is thus within reach and this remark also holds true for molecular organic solvents.

Quite recently, hydrophobic DES were used for liquid/liquid extraction of metals [18–20] but DES also display some ecotoxicological concerns [12].

Supercritical CO₂ and water are definitively green, provided no deleterious compounds are added [21].

Polyethyleneglycol and polypropyleneglycol are also green alternatives [9,12] but they are mainly used for extraction of biological compounds. Polydimethylsiloxane [9] might also be interesting but, to the best of our knowledge, has not yet been used for extraction.

Switchable solvents are a new and very elegant solution [22,23] based on the amine property to switch from a molecular neutral liquid compound, immiscible with water, to a salt easily soluble in water by water addition and CO₂ bubbling. Then, argon bubbling or heat recover the amine as a water-immiscible liquid.

Finally, one way to tackle the difficulty of finding green organic solvents non-miscible to water in view of liquid/liquid extraction would be to avoid water at the first place [24] but this solution still relies on the environmental impacts of the two immiscible solvents used. Another idea is to use aqueous biphasic systems (ABS) [25], especially with the introduction of acidic ABS [26–28].

Examples

Phosphor lamps

Phosphor lamps are one of the technological objects containing rare earths (RE), together with permanent magnets, batteries, flat panel displays etc. [29]. This family of elements was thrown at the front of the stage following the “rare earth crisis”. However, the composition of lamp

phosphor, as a source of Y, Eu, Tb but also of La, Ce and Gd, [29–32], and the market evolution towards LED which do not contain Tb and ca. a factor of ten less Y and Eu than linear fluorescent lamps [33], make recycling of these objects a challenging task [29] and a risky business [33].

Reviews on the recycling processes of phosphor lamps can be found in [29,32]. From these, only two studies can be considered as partially green [31,34]. Shimizu et al. used supercritical CO₂ in which nitric acid and a small molar amount of tri-butylphosphate (TBP) are dissolved to quantitatively extract Eu and Y, in the form of a neutral lanthanide-nitrate-TBP complex [34]. Y, La, Ce and Tb were not extracted. Although encouraging, this study would require further work to find ways to recover elemental lanthanides and to recycle TBP and nitric acid. The treatment of the Tb-rich LaPO₄:Ce³⁺,Tb³⁺ phosphor has been performed via a leaching step with methanesulphonic acid, followed by liquid-liquid extraction (with xylene and/or a phosphorylated extractant) which leads to the recovery of mixed oxide [31].

Multilayer flexible (food) packaging

Packaging waste in EU is estimated ca. 80 million ton/year from which 17% are multilayer flexible packagings (MFP), used for cereals, biscuits, beverages etc. [35]. MFP have a complex structure and a highly variable composition (several polymers, inks, Al foil, cardboard, etc.) because manufacturing companies innovate at a high rate. A recent review on recycling methods highlights the complexity and, consequently, the poor efficiency of current methods [4]. In particular, the Al foil (ca. 5 % of the total mass of the packaging), is often recovered as insoluble Al salts that should next be transformed into elemental aluminum. All the described methods suffer from either low efficiency, high energy cost, use of large amounts of organic solvents (chloroform, toluene etc.), chemical or safety risk [4].

A possible breakthrough has been achieved using the switchable solvent N,N-dimethylcyclohexamine (DMCHA) to treat a unique and well-defined bi-layer MFP [36] and more recently, various 4-layer MFP [35]. Once the paper part of the MFP has been removed, the idea is to first dissolve all the non-metallic components of the MFP in the monophasic low polarity state of DMCHA. The Al foil is thus easily recovered as a solid residue. Then, adding water and CO₂, the polymeric compounds are no longer soluble in the high polarity amine aqueous solution and are easily separated. The last step is the regeneration of the water-immiscible DMCHA neutral form. Very satisfying results are obtained with the bi-layer MFP sample composed of Al and LDPE, with recovery yields above 99% and 93%, respectively [36]. The LCA analysis confirmed the reduction of environmental impacts as compared to other waste treatments, including landfill. The 4-layer samples display different dissolution kinetics. However, the inks and paints are recovered as a single phase. The recovered Al flakes could be reused in metallurgical applications [35]. DMCHA is recovered with its initial properties, while LDPE is partially degraded. The overall recovery yield is ca. 99%, with similar efficiencies for the Al and the polymer parts. From these results, a layout for a recycling pilot plant is proposed. However, the economic performance calculation might be somewhat optimistic, as acknowledged by the authors, especially because of the (environmental) cost of evaporating and condensing water [8].

Permanent magnets

Permanent magnets are found in computers, mobile phones, wind turbines, audio systems and cars. Considering the differences in the time lags before these objects become wastes, prediction of the end-of-life fluxes is hard to make but RE recovery from such objects may reach significant percentages of the demand only after 2030 [37]. In the meanwhile, development of recycling technologies and dedicated infrastructures would be timely [37]. Usually, after strong mineral acids

leaching, selective and successive precipitation steps are favored [29,32] instead of liquid-liquid separations, often using of phosphorylated extracting agents [32].

The Binnemans group performed several very interesting works on the recycling of real NdFeB magnets [38–40], mainly differing by the leaching step: mineral acid [38], ILs [40] or DES [39]. This impacts the consecutive extraction steps: thiocyanate ionic liquid and phosphorylated extractant in toluene [39], chloride-based IL [38] or change in temperature to induce the biphasic state [40]. Finally, precipitation is always performed with oxalic acid. The great care dedicated to the recycling of all chemicals [40] and the scalability [39] should be commended.

Used tyres

Car tyres contain natural and synthetic rubber, carbon black and many other compounds. Although some used tyres are recycled into cement, a wiser way is to recover oil and gaseous compounds from a liquefaction process thanks to supercritical water [41], possibly adding natural coal as a synergist [42]. The maximum conversion yield amounts to only ca. 66% [42] and the liquid and gaseous products (kerosene, gasoline, CH₄, C₄H₁₀ etc.) would require further separation from one another but these results are inherently more promising than previous studies using hexane or dichloromethane [43].

Conclusion

This mini-review pinpoints two challenges: the use of green solvents and the need to adapt recycling processes to the ever changing nature and composition of wastes. For example, WEEE are hard to define, partly because of an increasing variety of connected objects [2,5,44], connected socks being one of the last innovations in this moving field. In the near future, new focuses will emerge, such as butts. Extending the definition of urban wastes [45], one could also worry about industrial process residues, mine tailing [46] or waste waters [47], that are clearly of environmental concern, and may gain importance as the metallic content of exploitable ores will keep decreasing. In addition, a better management of fluxes towards incineration plants would be useful [48].

Recycling obviously needs incentive of different kinds. Alerts about humanity survival are not enough, and in 2015 a plea was written for a balance between public subventions and market impulse, based on the Rhodia/Solvay experience in France for phosphor lamp recycling [33]. Unfortunately, business as usual won the game, as the plant was shut down only a year after this academic support¹. One way could be to lower public subventions and vote laws.

Acknowledgments.

The financial support of BATRE-ARES project (ERAMIN/0001/2015) funded by ADEME and FCT is greatly acknowledged.

Annotations

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¹ <https://www.usinenouvelle.com/article/solvay-renonce-au-recyclage-des-terres-rares.N375935> (in French)

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