Combining phytoextraction and ecocatalysis: a novel concept for greener chemistry, an opportunity for remediation

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EDITORIAL

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Scientific evidence shows that ecosystems are under unprecedented pressure, threatening prospects for sustainable development. The long history of mining operations has led to the accumulation of trace elements (TE) in the environment. Metal releasing is estimated to be 22,000 tons of cadmium, 939,000 tons of copper, 783,000 tons of lead and 1,350,000 tons of zinc in the environment for the period of 1950–2000. The problem is extremely important for different reasons: soils, floodplains, fields and rivers are contaminated. Environmental issues are inevitably following health issues when human population end up being exposed to heavy metal pollution: nervous diseases, kidney or lung malfunctions and bone malformations are clearly linked with heavy metal exposure. TE are persistent in ecosystems and living organisms. They are not biodegradable and tend to get increasingly concentrated in living organism along food chains in the magnification process. The high toxicity of TE in soil, water resources, and crops affect public health.

The overall impact of mining on ecosystems is serious. Technical feasibility and costs obviously limit soil remediation initiatives: in the case of metal pollution, the conventional method is excavation followed by burial of a waste site for an estimated cost of US$400,000 per treated hectare. Long-term solutions with lower operating costs are increasingly taken into consideration: phytoremediation appears as a sustainable technique to reclaim land. The ecological solution means public acceptance.

In spite of their toxicity, heavy metals can also exert a selective pressure on living organisms and thus drive

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evolution. Metal-tolerant plant species are able to grow on metal-contaminated soils while metal hyperaccumulating plant species can extract, transport and concentrate metals from soils into their above-ground parts. By definition, a hyperaccumulator accumulates at least 100 mg kg^{-1} of Cd, As and 1000 mg kg^{-1} of Co, Cu, Cr, Pb or Ni and 10,000 mg kg^{-1} of Mn or Zn (mg kg^{-1} are also often referred to as parts per million or ppm; ppm is the unit conventionally used in ecology while mg kg^{-1} is the unit in the international system—mg of metal are measured per kg of dry vegetal matter). About 450 metal hyperaccumulators have been discovered throughout the world.

In the south of France, former mines around Saint-Laurent-Le-Minier host a unique biodiversity: the ecotype of *Noccaea caerulescens* from Ganges was found to accumulate Zn and Cd with levels above 10,000 mg kg^{-1} of Zn. As they successfully adapted, endemic metal hyperaccumulators could be a tool to remediate metallic trace element pollution: more recently, *Anthyllis vulneraria*, a legume species as well as a zinc hyperaccumulator has showed potential for phytoextraction in Gard. This is a rare species to be both a leguminous and a metal hyperaccumulating plant. Therefore, the first utilization of *A. vulneraria* in phytoextraction is proposed.

In New Caledonia, the context is different. The island is estimated to account for 20 to 25 % of the world nickel resources. Industrial activities around nickel account for 10 % of the island's gross domestic product and could increase to 30–40 % in the upcoming years. New Caledonian mines are opencast, and before exploitation starts, vegetation, topsoil and upper soil horizons were removed. High-grade ores such as garnierite or saprolite are becoming scarce; new low-grade lateritic ores are being used with larger excavations. This inevitably leads to increased waste production in ore processing. Thus, the overall impact of mining on ecosystems is serious, with perturbations on water flows, soil erosion, contaminated sediment transport and bioaccumulation issues. Phytoremediation has a high potential in New Caledonia: the island is a metallophyte flora hotspot with 2,153 species (83 % endemics) identified on ultramafic soils. Twenty-seven past experiences in phytoremediation have been reported: 52 programs mainly considered species selection and agronomic techniques for the development of a sustainable plant cover on mine sites. Nickel and manganese phytoextraction was not considered, because a considerable limit of phytoextraction remained. This phytotechnology generates a new waste: contaminated biomass. It only shifts the metal contamination issue from soil to biomass and without credible outlets of contaminated biomass; phytoextraction will not be fully developed. Plant ashes with low metal content are to be considered as problematic phytotoxic waste, a serious drawback of energy production from contaminated biomass. In phytomining, metal hyperaccumulators have been considered as a 'bio-ore'. But, it has led to an economic failure.

This special issue of ESPR describes an innovative alternative which is to use the contaminated biomass to produce green catalysts. It is conceptually very different from phytomining and could overcome the limits of this technology.

Taking advantage of the adaptive capacity of particular plants to hyperaccumulate the transition metals in its aerial parts, it is possible to address the direct use of metals derived from plants as supported catalysts in organic chemistry. Plants and metallic wastes are directly recovered and transformed into green catalysts. The original polymetallic systems serve as heterogeneous catalysts in synthetic transformations allowing access to molecules with high added value for fine and industrial chemicals. The approach opens greener and broader perspectives in terms of new environmental and socioeconomic challenges.

Grison et al. are the pioneers in turning plants and metallic wastes into a resource through innovative technologies, processes and services. In this issue, authors are revealing that recycling wastes of plant and mine tailings constitute the starting point of an unprecedented concept in chemistry, namely 'ecocatalysis'. The development of this new concept is creating a paradigm shift in sustainable and green chemistry: metallic wastes are becoming new ecofriendly and efficient catalytic systems.

At the present time, combining phytoextraction and ecocatalysis is emerging as a promising strategy for developing new and valuable reactions. It has also attracted considerable attention as it enables unprecedented transformations that are not possible by using transition metal complex or organocatalyst. The results are the first use of biomass derived from phytoextraction in organic synthesis. They constitute an encouragement for the economic development of phytoextraction and remediation programs for metal-bearing soils. The use of zinc-, nickel- and manganese-enriched biomass to produce ecocatalysts used in organic syntheses could bring change and spur the development of phytoextraction.

In this special issue, the innovative approach is illustrated with recent outstanding examples developed in Opportunity E^4 ANR program, with the aim of shedding light on the synthetic utilities and potentials of this concept as a novel tool in organic synthesis.

Mutually, the zinc, nickel and manganese phytoextraction is described to field-scale trials on mining sites in the south of France and New Caledonia, respectively. Results clearly demonstrate the potential for such trials that would clearly promote remediation and rehabilitation of contaminated soils on mine sites.

The combining of phytoextraction and ecocatalysis is an Environmental, Ecological, Ethic and Economic (E^4) Opportunity.

Claude Grison is a Professor of Bioorganic Chemistry at the University of Montpellier. She is the lead of the laboratory of 'Bio-inspired Chemistry and Ecological Innovations'. Since 2008, she chose to develop a new domain in the Ecology-Chemistry Interface. New domains of expertise were also developed like bacterial stress and plant biotechnology and more recently new chemical recovery of phytoremediation based on a novel concept of green chemistry, called 'Ecocatalysis'. She was also an expert for the Higher Education of the Ministry for Education and Research, CNRS (French National Centre for Scientific Research) and National Museum of Natural History (MNHN) and the National Research Alliance for the Environment, AllEnvi. She has published more than 136 papers and patents, presented 73 conferences and 152 communications. She has received 8 awards for Innovative Technologies and the concept of the ecocatalysis, the most recent being the Innovation Award of CNRS.