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Soil Remediation Technologies towards Green Remediation Strategies

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***Abstract*—**As a result of diverse industrial activities, pollution from numerous contaminant affects both groundwater and soils. Many contaminated sites have been discovered in industrialized countries and their remediation is a priority in environmental legislations. The aim of this paper is to provide the evolution of remediation from consolidated invasive technologies to environmental friendly green strategies. Many clean-up technologies have been used. Nowadays the technologies selection is no longer exclusively based on eliminating the source of pollution, but the aim of remediation includes also the recovery of soil quality. "Green remediation", a strategy based on "soft technologies", appears the key to tackle the issue of remediation of contaminated sites with the greatest attention to environmental quality, including the preservation of soil functionality.

***Keywords*—**Bioremediation, green remediation, phytoremediation, remediation technologies, soil.

I. INTRODUCTION

THE remediation of contaminated sites is essential for the protection of environmental resources and human health. The development of technical tools for site remediation is one of the key objectives of the EU environmental policy. Therefore, in recent years, special attention has been devoted to soil protection, and the European Community has produced specific documents to recognize the environmental, socio-economic and cultural soil functions. In 2002, a communication entitled "Towards A Thematic Strategy For Soil Protection" (COM(2002)179) was developed and followed by the "Soil Thematic Strategy" (COM(2006)231) and by the proposal for a "Soil Framework Directive" (COM(2006)232), still not approved [1], [2]. Erosion, loss of organic matter, compaction, salinisation, landslides, sealing and contamination have been identified as the main causes of soil degradation. However, soil contamination is difficult to quantify, especially because national inventories of contaminated sites, envisaged by the proposed "Soil Framework Directive", are still not a reality across Europe. These tools have started to recognize the environmental, socio-economic and cultural soil functions.

Recent estimates of the European Commission reported a total of about 2.5 million potentially contaminated sites and about 342.000 sites really contaminated, in European countries [3]. The difficulties in obtaining accurate data are also due to the differences in the soil status definition and interpretation among countries. The European Environment Agency (EEA) has proposed a distinction between "Contaminated site" and "Potentially contaminated site" to try to minimize this complication. The first is defined as "a well-defined area where the presence of soil contamination has been confirmed and this presents a potential risk to humans, water, ecosystems, or other receptors. Risk management measures (e.g., remediation) may be needed depending on the severity of the risk of adverse impacts to receptors under the current or planned use of the site". The definition of potentially contaminated site refers to "sites where unacceptable soil contamination is suspected but not verified, and detailed investigations need to be carried out to verify whether there is unacceptable risk of adverse impacts on receptors" [3], [4].

A wide range of remediation technologies are available on the market and they differ substantially in terms of: i) the method they use, ii) the environmental impact, iii) the cost, and iv) the time to complete the remediation. In accordance with the Directive 96/61/EC (Concerning Integrated Pollution Prevention And Control), repealed by the most recent Directive 2010/75/EU (on Industrial Emissions, Integrated Pollution Prevention And Control), for identification and selection of the best technical intervention (BATNEEC- Best Available Technology Not Entailing Excessive Costs), it is essential to define the desirable level of environmental protection. The selected technique should be the most reliable to achieve and to maintain the desired security levels, considering, at the same time, the management and monitoring costs. In recent years, to address the problem of soil contamination, US Environmental Protection Agency (US-EPA) has proposed the new concept of "Green Remediation", in which there is the integration of the green technology and sustainable recovery concepts of contaminated sites [5], [6]. Contaminated sites management issue is moving towards a synergy among environmental, economic and social aspects.

The aim of this paper is to provide an overview of the main remediation technological approaches currently available, and of the possibility to move towards green remediation strategies in Europe.

II. SOIL REMEDIATION CONSOLIDATED TECHNOLOGIES

Remediation technologies can be subdivided into categories based on their action (Table I).

Excavation and landfilling cannot be strictly classified as a technology but it is still one of the most used solution. However, the reduced landfill availability and the environmental constraints, forced EU legislation to promote a drastic reduction in the use of landfill.

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TABLE I
THE TARGETS OF CLEAN-UP TECHNOLOGIES

- ✓ Destruction of contaminants
- ✓ Mobilization and recovery, using treatments that transfer contaminants from polluted soil to another matrix from which contaminants are subsequently recovered
- ✓ Transformation of pollutants into less dangerous or harmless products
- ✓ Inertization and/or immobilization by processes that make in the contaminated site pollutants inert or less mobile
- ✓ Excavation and landfilling of contaminated matrix

The processes of soil clean-up must be preceded by a careful study of the main soil characteristics. In particular, it is necessary to take into consideration those characteristics that influence the movement of water, infiltration, permeability etc. …, and the properties that affect the mobility of the contaminants. It is also essential to consider the properties of contaminants that influence their behavior and fate in the soil because these properties will help to identify the kind of treatment that will be necessary to tackle the pollution from each particular class of substances.

The remediation processes can be further classified as "*ex-situ*" or "*in-situ*". The "*ex situ*" technologies are based on a preliminary removing of the contaminated soil and a following treatment in proximity of the involved area (on-site) or in external treatment plants (off-site). The "*in-situ*" technologies are applied directly to the contaminated site without movement or removal of the polluted soil.

The main advantages of "*in situ*" technologies are that they can operate with reduced environmental impacts and without costs associated with excavation. The main drawbacks are related to the difficulties in ensuring that the contaminants are effectively reached by the technologies due to heterogeneity of soil and the uncertainty in the distribution of contaminants. These problems related to the complex nature of the soil make also difficult to verify the performance of the technologies in terms of remediation target. To overcome this problem, it is necessary a detailed characterization of the site, and to determine the contaminant properties and behaviour in that specific site. "*In situ*" technologies require treatability test to evaluate their efficiency at a specific site. "*Ex situ*" technologies are applied to excavated soil. The main advantage of these technologies is that contaminants may be fully accessible to treatment processes by intimate mixing of reagents and contaminants. The process may be implemented and optimized, with a final easier verification of the clean-up efficiency. The timescales for "*ex situ*" remediation is typically much shorter than for "*in situ*" remediation. Several contaminated sites require more than one treatment to reach clean-up goals and different technologies may be combined (train technology) to obtain the requested efficiency.

The remediation technologies can be schematically divided into different categories: physical, chemical, biological, thermal, and inertization (Table II). However, the same technology may belong to different categories such as the vitrification process which can be considered both a thermal or inertization treatment.

Detailed descriptions and more information on each technology can be found on the site of EPA [6]

TABLE II
REMEDIATION TREATMENT TECHNOLOGIES

- ✓ Physical treatments employ physical processes and are used with the aim to isolate or concentrate the pollutants. Physical treatments do not destroy the contaminants, they are often used as the first stage in clean-up processes, in which several decontamination technologies are used
- ✓ Chemical treatments are designed to remove or destroy the pollutants, or to change their structures in other less environmentally hazardous by appropriate chemical reactions between the contaminant in the soil and an appropriate chemical agent
- ✓ Biological treatments are based on the ability of microorganisms to degrade the molecules of organic contaminants and to use them as a source of nutrients
- ✓ Thermal treatments are designed for the thermal destruction of the most of the organic contaminants present in the soil. Depending on the temperature may be used also to immobilize the contaminants (vitrification)

III. GREEN REMEDIATION STRATEGY

The use of consolidate technologies (Table III) has often underestimated both negative environmental impacts, such as wastes production, energy consumption, and beneficial opportunities for the economic growth and the social acceptance. New approaches to remediation will be required if soils have to perform their essential functions. There is a need to find new strategies of remediation as alternative to rather drastic technologies or soil removing and landfill disposal. Nowadays there is a growing interest in the clean-up approaches that restore contaminated sites to productive use with a great attention to the global environmental quality, including the preservation of soil functionality. This new strategy is defined by the US-EPA as "Green Remediation: the practice of considering all environmental effects of remedy implementation and incorporating options to minimize the environmental footprints of clean-up actions" [6]. Core elements of "Green Remediation" are reported in Table IV.

Usually, green strategies addressed to the use of Best Management Practices (BMPs) that reduce the negative impacts on the surrounding environment during operation of the remedial action [7].

EPA [6] identified some key elements to be considered in selecting the best technologies (Table V).

A complete green strategy should also include an analysis of LCA (Life Cycle Assessment) to demonstrate the low environmental impact. This process allows to identify the economic and social effects at all stages of the process in addition to the environmental aspects. EPA has defined a roadmap to evaluate the environmental footprint of remediation projects with the aim of providing information useful for adjusting the project's operating parameters to reduce the footprint.

In "Green Remediation" soil quality is no more evaluated in terms of generic values of total contaminant concentrations, and the allowable residual concentration in soil is determined only by a site specific risk assessment procedure. It is essential to consider the wastes that will be generated and the percentage that may be reused, the amount of water to be used, the fate of water after use, and the protection of the ecosystem, including soil, that are affected by the remediation technology selected.

TABLE III
SOME OF THE MOST USED TECHNOLOGIES APPLICABLE TO EACH CONTAMINANT CLASSES

Inorganic Contaminants	*In Situ*	*Ex Situ*
Metals and Inorganic Compounds	Phytoremediation (B) Soil Flushing (C/P) Stabilization/ Solidification (S/S) Electrokinetics (C/P)	Chemical Extraction (C/P) Chemical Oxidation/ Reduction (C/P) Soil Washing (C/P) Stabilization/ Solidification (S/S) Solvent Extraction (C/P)
Explosives	Bioremediation (B) Phytoremediation (B)	Bioremediation (B) Soil Washing (C/P) Solvent Extraction (C/P) Thermal Desorption (Th)
Petroleum Fuel Oil	Bioremediation (B) Soil Vapour Extraction (C/P)	Bioremediation (B) Soil Washing (C/P) Thermal Desorption (Th)
Organic Contaminants	*In Situ*	*Ex Situ*
Aromatic Hydrocarbons and PAHs	Bioventing (B) Bioremediation (B) Phytoremediation (B) Thermal Treatment (Th)	Biopiles (B) Composting (B) Landfarming (B) Bioreactors (B) Thermal Desorption (Th) Incineration (Th)
Halogenated or Chlorinated Aliphatic Hydrocarbons	Bioventing (B) Bioremediation (B) Phytoremediation (B) Soil Flushing (C/P) Soil Vapour Extraction (C/P) Chemical Oxidation (C/P) Thermal Treatment (Th)	Biopiles (B) Bioreactors (B) Thermal Desorption (Th) Incineration (Th)
Chlorinated/ Non-Chlorinated Phenols	Bioventing (B) Bioremediation (B) Phytoremediation (B) Soil Vapour Extraction (C/P) Thermal Treatment (Th)	Biopiles (B) Composting (B) Landfarming (B) Bioreactors (B) Thermal Desorption (Th) Incineration (Th)
Dioxins and Furans	Thermal Treatment (Th) Phytoremediation (B) Bioremediation (B)	Stabilization/ Solidification (S/S)

B=Biological Processes; C/P=Chemical/Physical processes; Th=Thermal processes; S/S=Stabilization/Solidification processes.

TABLE IV
FUNDAMENTALS OF "GREEN REMEDIATION"

- ✓ Use minimally invasive technologies
- ✓ Use passive energy technologies such as bioremediation and phytoremediation as primary remedies or in finishing steps where possible and effective
- ✓ Minimize soil and habitat disturbance
- ✓ Minimize bioavailability of contaminants

In "Green Remediation" projects, Bioremediation and Phytoremediation are among the most used technologies.

Bioremediation technologies are based on the natural capability of microorganisms to breakdown organic contaminants utilizing these molecules as a source of food and energy. A basic prerequisite for the activation of these processes is the presence in the contaminated soil of adequate levels of moisture and of oxygen, necessary to optimize the natural biochemical mechanisms, which lead to the degradation of the organic compounds. The main advantages of these technologies include the possibility to treat a wide range of organic contaminants, in different environmental matrices, the absence or a reduced production of waste, and lower costs if compared with other technologies. However, bioremediation is highly dependent on the characteristics of the site, thus it requires a very thorough site characterization and long treatment times. Nearly all organic contaminants including BTEX (benzene, toluene, ethylbenzene, and xylenes), PAHs (polycyclic aromatic hydrocarbon), PCBs (polychlorinated biphenyl) may be treated with bioremediation technologies if in soil, oxygen, moisture, nutrients and temperature are adequate for microbial growth to perform aerobic biodegradation [8]-[10].

TABLE V
KEY ELEMENTS IN "GREEN TECHNOLOGY" SELECTION

- ✓ Energy: minimize total energy use and increasing the percentage of energy from renewable resources
- ✓ Air and atmosphere: minimize air pollutants and greenhouse gas emissions
- ✓ Water: minimize water use and impacts to water resources
- ✓ Material and waste: improving materials management and waste reduction efforts
- ✓ Land and Ecosystem: protect land and ecosystems during site clean-up

Bacteria and fungi are the main agents of bioremediation. Organic molecules may be degraded by a single type of microorganism but frequently the combined action of multiple organisms increase the decontamination efficiency. Organic contaminants are characterized by a wide spectrum of functional groups, with different chemical properties, and microorganisms with specialized metabolic abilities should be used to degrade specific contaminants. The biodegradation pathway may lead to the production of metabolites that can be less (or even more) toxic of the parent compound. The ultimate goal of the biodegradation process is complete mineralization of the organic contaminants, resulting in carbon dioxide, water and cell biomass without accumulation of by-products [11]. In this case the requisites of "Green Remediation" are completely satisfied [6].

The success of bioremediation greatly depends on the contaminants bioavailability. Bioremediation is sometimes limited because compounds are insoluble, or irreversibly sorbed on soil surfaces, and can be degraded only after dissolution in the soil aqueous phase. Therefore, bioavailability must be considered at each specific contaminated site. In soil, the bioavailability is the resultant of a series of complex mechanisms of mass transfer and retention-release, which are determined by the properties of the contaminants, the chemical-physical characteristics of the soil and the biology of the plants [12], [13].

Bioremediation may be based on spontaneous degradation activity of microorganisms without any external modification, or may be "engineered" [14] to accelerate the contaminant removal efficiency by promoting microorganisms' activity through a modification of chemical and physical soil parameters (e.g. oxygen, nutrient content, pH etc.)

Preliminary studies at lab-scale are necessary. The success of this technology strongly relies on characterization and monitoring before and during the remediation process [15].

Phytoremediation includes several technologies that use plants for remediation of soils, sediments and contaminated water, exploiting the natural ability of plants to accumulate, or immobilize the contaminants [16]. Plants promote degradation by microorganisms of organic compounds providing carbonaceous substrates and oxygen. Positive results have been obtained in soil polluted by many organic compounds including total petroleum hydrocarbons (TPH), PAHs, PCBs, organophosphate insecticides, surfactants and radionuclides [17].

Among phytoremediation technologies, the most promising and innovative was considered heavy metals phytoextraction. Phytoextraction originates from the study on soils rich in heavy metals were specific plant species defined hyperaccumulators are able to grow and to uptake high amounts of metals from the soil through the root system and to concentrate them in the aerial part [18]. The translocation of the metal from the soil to the plant allows the removal of the contaminant "*in situ*" with plants harvesting. In addition to hyperaccumulators, also other species are employed mostly for a soil shallow decontamination (30-100cm), increasing their ability of contaminants accumulation, after modification of the soil chemical conditions [12], [13]. Tree species may be used where pollution is located in deeper soil layers [19].

The efficiency of the technology is strictly dependent on the assessment of bioavailability of contaminants. Phytoextraction may be successfully used to remove the amount of metals that are bioavailable or may be made bioavailable [20], [21] fulfilling in this way one of the main objectives of "Green Remediation", the reduction of bioavailable pollutants [22].

Phytoremedition has the advantages of low costs, low energy consumption and low impacts on the environment. The main limitation is the time required to complete the decontamination process. The produced biomass may be not considered as waste since it may be used for energy production or as a source of recyclable metals.

IV. TOWARDS THE FUTURE

The remediation of contaminated soils started at the end of the '70 using consolidates technologies (incineration inertization etc.) previously employed in waste treatment. This has contributed to consider a contaminated soil as a hazardous waste. Unfortunately, this rough approximation was transferred in many legislations and soil knowledge have been used only marginally in the clean-up procedures. For many years' soil quality has been defined by a value of concentration of a contaminant and excavation and landfill disposal of soil has been largely used. In the last years the knowledge of remediation technology has rapidly grown. At present many treatment processes appear to be really feasible at field scale, and soil remediation is now based on risk assessment procedures. Innovative technologies, largely dependent on soil properties, such as *in-situ* chemical oxidation, electroremediation, bioventing, soil vapor extraction etc. have been successfully applied. Hazardous organic compounds are commonly treated by biological technologies, bioremdiation and phytoremediation, being the last applied also for metals. Technologies selection is no longer exclusively based on eliminating the source of pollution, but also on blocking the pathways from contaminants to receptors or reducing the exposure to contaminants. There is a growing interest in the clean-up approaches that maintain soil quality after remediation treatments. "Green Remediation" appears the right strategy that restores contaminated sites to productive use with a great attention to the global environmental quality, including the preservation of soil functionality. If we move from the current definition of remedial targets based on total concentrations, technologies with low impact on the environment can be utilized thus reducing the soil disposal in landfill, avoiding to destroy a not renewable essential resource.

To further encourage the green technologies choice, still much work in regulatory and communicative field needs to be done. The introduction of administrative facilities, guidelines and protocols might represent the right tools to promote these innovative techniques acceptance.

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