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Dual Soil Decontamination Procedures

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Abstract

Pollutants actually existing in various types of soil, ranging from rural, agricultural soils to urban or factory soils, belong to a wide range of chemical compounds, both organic and inorganic. The modern decontamination methods were each specifically designed for a particular pollutant. Reagents and procedure conditions targeted only one particular contaminant, more rarely several pollutants, all usually belonging to the same family (e.g., several heavy metals or polychloro-*p*-dibenzodioxins and polychloro-*p*-dibenzofurans). Most reviews on the subject presented soil decontamination processes under the same auspices: specific process with specific reagent for a specific pollutant. Unfortunately, soils are often cross-contaminated with various types of pollutants, which make the decontamination procedure much more complicated: indeed, for each contaminant, a certain procedure must be carried out. This transforms the whole decontamination process in a multi-step procedure, enhancing the costs. Therefore, any method that could realize a simultaneous decontamination for at least two different types of pollutants would be extremely advantageous. In the recent years, such methods made an interesting appearance in the environmental science and engineering literature. We wish to review these dual decontamination methodologies that deal simultaneously with at least one organic and one inorganic contaminant in the same soil matrix.

Keywords: simultaneous decontamination, heavy metals, pesticides, dioxins

1. Introduction

Over two centuries of various anthropogenic emissions have caused soil contamination to be a globally widespread problem, involving not only industrialized countries but even remote areas of less developed countries [1]. From decision makers to scientists and even to individual

citizens, all generally accept and understand that air and water pollution can have negative impacts on human health [2–4]. However, the same statement concerning soil pollution is harder to understand [5]. In the vast majority of papers or books that deals with the problem of soil pollution, the traditional approach is to isolate a single variable, such as a specific contaminant, and then investigate that variable as its source, fate, distribution and/or health effect [6]. Nonetheless, it is difficult to accept that, after 200 years of industrialization and intensive agriculture, rural and urban soil are only mono-contaminated. It is more than probable that in any contaminated soil horizon, more than one pollutant is present [7]. Among the most common harmful contaminants are heavy metals (37%) and mineral oils (33%), along with a large variety of persistent organic pollutants (known as POPs). Scientists and members of the medical professions are acknowledging that environmental and health effects due to soil multiple contamination present complicated issues due to synergistic relationships [8].

Almost all manuscripts that presented soil decontamination techniques have a similar approach: identification of a single pollutant and subsequent treatment. Moreover, the vast majority of these studies generally use a clean soil spiked with the chosen compound. The general reason given for not using genuine contaminated soil is often the same: since it is known that many remediation processes belong to either phyto- [9] or bioremediation [10] families, the authors wanted to avoid interferences with their own method. However, such procedures may be valuable in diminishing or even completely eliminate a particular pollutant, but in the probable case of multiple contaminations it would mean a multiple treatment of the polluted soil. Moreover, most of these treatment methods are still on the laboratory or on the *ex situ* scale [11]. This renders most of the laboratory-scale treatment inapplicable because of ultimately high costs: the same soil should be treated in various ways, according to each particular pollutant present [12, 13].

The general assessment criteria for the selection of the proper remediation technology are:

- the short-term versus long-term effectiveness in remediation;
- the reduction in mass or volume of the contaminants (preferably their complete eradication);
- the overall reduction of the toxicity of previously contaminated soil; and
- the cost-effectiveness.

Thus, in order to diminish the costs of a treatment procedure applied to contaminated soils, an obvious solution would be to have *in situ* treatment instead of an *ex situ* one (completely removing the cost of transportation and relocation of soil). A good number of such processes are also known nowadays [14–17].

There are various ways to consider the most appropriate way to treat a contaminated soil [11]. These are the following: (1) doing nothing (if the environmental assessment indicates that humans and the environment are not at risk, then no remediation activity is required, e.g., in the case of small-scale spills on sites where human and animal exposure is not likely), (2) introducing institutional controls to contain the contaminants in the infected area (a legal or institutional mechanism that limits the use or the access to the contaminated area, e.g., the Chernobyl or Fukushima areas) or (3) the removal of soil and/or destruction of contaminants

(in some cases, the best option may be to physically remove the contaminated soil and move it to a special treatment, storage and disposal facility; in other cases, it is possible to remove the contaminant from the soil using technologies such as surfactant washing, soil washing or thermal desorption). Ultimately, the contaminants are destroyed, on condition that the by-products are not toxic.

The *in situ* technologies are categorized into three major groups based on the primary mechanism by which the treatment is achieved:

- Physical/chemical
- Biological
- Thermal

Physical/chemical treatment includes soil vapour extraction, solidification/stabilization, soil flushing, chemical oxidation and electrokinetic (EK) separation. Biological treatment uses microorganisms or vegetation to degrade, remove or immobilize pollutants in soil. Biological technologies include bioventing, phytoremediation and monitored natural attenuation. Electrical resistivity heating, steam injection and extraction, conductive heating, radio-frequency heating and vitrification are technologies summarized under thermal treatment.

The past few years saw an increase in the number of *in situ* treatment technologies that are effectively used in the field (e.g. chemical oxidation [18] or thermal treatment [19]), demonstrating thus that *in situ* technologies are a viable option for treating contaminated soils.

Yet, in order to have a truly useful as well as an economical process, the technology should be able to eliminate more than only one contaminant, simultaneously, since it is obvious that mono-pollution is an utopian case. For example, the soils of abandoned agricultural land contaminated by e-waste activities in Hong Kong listed no less than four classes of pollutants (polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls, polybrominated diphenyl ether compounds and heavy metals—cadmium, copper, chromium, lead and zinc) [20]. Fortunately, in the last few years, such methods made an interesting appearance in the environmental science and engineering literature. In the following, we review some of these dual decontamination methodologies that deal simultaneously with at least one organic and one inorganic contaminant in the same soil matrix.

2. Procedures for simultaneous decontamination of polluted soils

This chapter presents a review of the processes and technologies that allow the simultaneous removal/destruction/immobilization of more than one class of contaminants in soils, focusing on dual decontamination of at least two different pollutants, one being an inorganic, the second an organic compound. Relevant papers were retrieved using screening of the scientific literature using Scopus, ISI Web of Knowledge and Google Scholar.

As previously mentioned, the most important class of inorganic pollutants is represented by heavy metals [21], while among the organic pollutants various classes of compounds can be

mentioned [22] (e.g. pesticides, polyaromatic hydrocarbons, polychlorinated compounds, etc.) and it is more than often that either rural or urban soils are polluted with both types (organic and inorganic). In order to realize a simultaneous cleansing of the soil, the method used must be suitable and effective for both classes of compounds. Indeed, some of the methods applied separately for organic or inorganic contaminants proved to be successful when both types of compounds were present in soils. These methods can be classified as follows:

- Washing using a proper solvent mixture and eventually a surfactant (including flotation processes)
- Electrokinetic methods (derived from the washing techniques)
- Bioremediation (including phytoremediation)
- Combinations of the previous
- Miscellaneous (including thermal or chemical methods)

2.1. Washing processes

Chronologically speaking, elution techniques were the first used to simultaneously clean contaminated soil with both heavy metals and organic compounds, as early as the end of the twentieth century. The main problem was identifying the proper solvent mixtures.

One of these early papers in the field of dual separation techniques investigated the ability of aqueous cyclodextrin solutions to simultaneously remove heavy metals and low-polarity organic compounds from contaminated soil [23]. In that purpose, Brusseau and co-workers used three types of soil spiked with the model organic compound (phenanthrene) and the model heavy metal (cadmium). Previously, Dunn et al. had used surfactants in a micellar-enhanced ultrafiltration, which is a separation process using surfactants and membranes, removing dissolved organic solutes or multivalent ions from water with high rejections [24]. Through this procedure, mixtures of pollutants containing phenol or *o*-cresol and Zn^{2+} and/or Ni^{2+} were separated from contaminated soils, using an anionic surfactant. Micellar-enhanced ultrafiltration was subsequently used by other authors to remove either Cu and phenol [25] or chlorinated aromatic hydrocarbons, nitrate and chromate ions [26]. Modified cyclodextrin (as glycine- β -cyclodextrin) was later successfully used in the study of the desorption behaviour of phenanthrene and lead from co-contaminated soil [27]. The authors showed that glycine- β -cyclodextrin had good solubilization properties for both phenanthrene and lead carbonate (900 g/L for phenanthrene, respectively, 2945 mg/L PbCO_3).

A parallel process used a combination of 2.5 N sulphuric acid and isopropyl alcohol (in a 4:9 ratio), with a dilution of 5 part solution to 1 part soil, the separation being made by ultrafiltration [28]. The contaminants removed in these experiments were heavy metals (Cd, Ag and Cu), volatile organic compounds (ethyl benzene and methyl iso-butyl ketone), halogenated compounds (chloroethene and tetrachloroethylene) and pesticides, herbicides and insecticides (lindane, methoxychlor and endrin). However, the acidic treatment cannot be applied to other types of soils than sandy ones. The ultrafiltration methods are still at the laboratory-scale level

and therefore are not yet suitable for *in situ* applications. Thus, researchers tended to deepen the knowledge in the field of surfactant use.

A first step was to widen the variety of surfactants used. Thus, Marshall and co-workers, after testing the efficiency of a non-ionic surfactant (polyethylene oxide (PEO) of chain length 7.5 (Triton X-114), 9.5 (Triton X-100), 30 (Triton X-305) or 40 units (Triton X-405)), combined with iodide salts [29], introduced the use of ethylenediaminetetraacetate (EDTA) to simultaneously extract heavy metals and polychlorinated biphenyl compounds from a field-contaminated soil [30]. Since both cyclodextrin and EDTA were effective, the use of their combination was a naturally occurring step, took again by Marshall and his team at the McGill University [31]. Thus, ultrasonication was used to mix field-contaminated soil with a combination of cyclodextrin solution (10%, w/v) and 2 mmol EDTA, in the same time mobilizing polychlorinated biphenyls and much of the metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn). The authors observed that a combination of randomly methylated or hydroxypropyle β -cyclodextrin with EDTA did not alter the polychlorinated biphenyls extraction efficiency nor did the presence of cyclodextrin change the efficiency of mobilization of most heavy metals (Al, Cd, Cr, Fe, Mn, Ni and Zn) but it did increase the recovery of Cu and Pb. Three sonication washings with the same charge of reagents mobilized appreciable quantities of polychlorinated biphenyls (40–76%) and quantitatively extracted the labile fraction of Cd, Cu, Mn and Pb. However, due to the low degree of biodegradability in soil [32], Marshall opted for another complexing reagent (ethylenediaminedisuccinic acid, [S,S]-EDDS). Thus, the same authors evaluated the efficacy of soil washing with a non-ionic surfactant (Brij98) in combination with [S,S]-EDDS for the simultaneous mobilization of heavy metals and polycyclic aromatic hydrocarbons from a field-contaminated soil [33, 34]. Moreover, they extended their procedure to the remediation of polluted soils with arsenic, chromium, copper, pentachlorophenol (PCP), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [35]. The highest level of mobilization/detoxification was achieved in three soil washes with a mixture of 0.1 M [S,S]-EDDS and 2% Brij98 at pH 9 with 20 min of ultrasonication treatment at room temperature. This combination mobilized 70% of As, 75% of Cr, 80% of Cu, 90% of pentachlorophenol and 79% of PCDDs and PCDFs.

In order to render the process even more environmentally friendly, many authors turned their attention to naturally occurring surfactants. Thus, starting from the idea that biosurfactants are potentially less toxic to soil organisms than other chemical agents, Lima and co-workers studied the efficiency of a combination of iodide salt ligands and surfactants produced by different bacterial species in the simultaneous removal of cadmium and phenanthrene in a Haplustox soil sample [36]. For their part, Zhu et al. from Zhejiang University used saponin, a plant-derived biosurfactant, for the dual removal of phenanthrene and cadmium from contaminated soils [37]. Another Chinese team successfully treated soils from a contaminated electronic waste site that contained both polybrominated diphenyl ethers and heavy metals using common sunflower oil in a mixture with carboxymethyl chitosan [38].

Another Canadian team, led by Blais from the Université du Québec, chose to combine alkaline-washing process with flotation in acidic solutions (in the presence of a surfactant such as cocamidopropyl betaine). They succeeded in decontaminating various types of soils from

mixtures of heavy metals, pentachlorophenol and polychlorodibenzo-*p*-dioxins and furans (PCDD/F) [39]. Blais' process is mainly based on physical techniques, such as crushing, gravimetric separation and attrition. In another such study, Blais' team demonstrated that it is possible to attain removal efficiencies of 49–73% for Cu and from 43 to 63% for Zn, whereas a removal yield of 92% was measured for total PAHs [40, 41]. The results were improved replacing cocamidopropyl betaine with cocamidopropyl hydroxysultaine (up to 90% PAHs and Pb removal, in three different polluted soil types) [42]. By carefully choosing the acidic species (hydrochloric, nitric, sulphuric and lactic acids and ethanol) for leaching metals from soil in combination with non-ionic, ionic and amphoteric surfactants, Blais and co-worker studied the simultaneous removal of heavy metals and pentachlorophenol by flotation [43]. Thus, removal yields of 82–93, 30–80, 79–90 and 36–78% were obtained from As, Cr, Cu and PCP, respectively.

A different approach was undertaken by a team from the Hebrew University of Jerusalem, under the form of a sediments remediation phase transition extraction [44]. This process is based on using partially miscible solvent mixtures in which specific organic soluble chelating agents are dissolved. Extraction efficiency is improved by a phase transition cycle induced by temperature variation. With this technology, up to 90% of cadmium ions were removed within approximately 15 min, as well as practically all the organic matter, including PAHs.

2.2. Electrokinetic processes

A second family of technologies that allow concurring decontamination of co-contaminated soils are the electrokinetics processes (*aka* electrokinetics). Electrokinetics are a group of emerging techniques that are intended to separate and extract heavy metals, radionuclides and organic contaminants from various types of soils, sludges, sediments and even groundwater [45]. The goal of electrokinetic remediation is to realize the migration of subsurface contaminants in an imposed electric field via electro-osmosis, electromigration and/or electrophoresis. These phenomena occur when the soil is electrically charged with a low-voltage current. The fundamental configuration for all three processes involves the application of an electrical potential between electrode pairs that have been implanted in the ground on each side of a contaminated soil mass. There are even some emerging *in situ* electrokinetic soil remediation technologies, such as Lasagna™, Elektro-Klean™ or Electrobioremediation.

Even from the first attempts to simultaneously eliminate both heavy metals (including lead, zinc, manganese, copper and arsenic) and organic pollutants (PAHs, benzene, toluene, ethylbenzene and xylene) from co-contaminated soils, it was clear that migration occurred on the straight line between electrodes and that the process is a lengthy one, from 23 to 112 days, using a current density of 3.72 A/m² [46].

Pioneering studies on electrokinetics were performed at the University of Illinois in Chicago by Professor K.R. Reddy whose results demonstrated the effectiveness of this method on soils polluted either with heavy metals [47, 48] or organic contaminants [49, 50]. In an obvious continuation, electrokinetics was applied to soils co-contaminated with both heavy metals and organic pollutants [51]. As required by the theory of electrokinetic remediation technologies, the soil was acidified, using 1 M citric acid, which acted also as a chelating agent, along with

ethylenediaminetetraacetic acid, and some surfactants (Igepal or Tween). The best results of the sequential extraction test were obtained with citric acid 1 M combined with Igepal CA-720 (5%) or Tween (5%). However, the authors observed that the presence of surfactants tended to reduce the electric conductivity of the soil and the electro-osmotic flow compared with the stages where citric acid was used as flushing solution. The results confirmed previous studies, in which the ability of surfactants, cosolvents, cyclodextrins, chelating agents and organic acids to remove Ni and phenanthrene from kaolin soil was tested [52, 53]. EDTA was confirmed to produce complications during electrokinetic experiments [54].

Surfactants, cosolvents and cyclodextrins (same as in washing technique) generally yielded better results for phenanthrene removal, whereas chelating agents and organic acids yielded better removal for Ni [55].

To some extent, the EK process can be applied to sediments of harbour waterways, for the rapid elimination of heavy metals (Cd, Cr, Cu, Zn and Pb) and PAHs [56]. Beside citric acid, nitric acid (which is not recommended in case of *in situ* remediation) was also tested to avoid the formation of an alkaline front into the sediment and favour the metals removal. As surfactants, sodium dodecyl sulphate (as an anionic surfactant) and Tween 20 (as a non-ionic surfactant) were used to solubilize and mobilize PAHs. However, for achieving an almost complete removal of heavy metals and PAHs, the process needs ca 10 days. The EK process was extended to real-life polluted soil, deriving from a dismissed industrial site, contaminated with several metals: Hg, Ni, Co, Zn, Pb, Cu, Cr, As and organic substances [57]. Using a Ti/Pt-Ir anode and a stainless steel cathode, the procedure allowed a fair to good removal of most of heavy metals and PAHs over an interval of 10–15 days. An addition to the previous procedure was the presence of an oxidizing leaching agent, electrochemically produced. A similar approach, by using an oxidizing agent such as H₂O₂ (hydrogen peroxide was also present in a study by Reddy and co-workers [58]), NaClO, KMnO₄ or Na₂S₂O₈ in a controlled pH (3.5 or 10), was applied in a so-called enhanced-EK remediation technology to decontaminate a heavy metal-organic compound co-contaminated soil [59]. Over ca 14 days of applying 1.0 V/cm, the results showed that there was significant migration of pyrene (favoured by the presence of oxidizing reagent such as KMnO₄ or Na₂S₂O₈) and Cu from the soil (favoured by low pH), and that the removal percentage of soil pyrene and Cu varied in the range of 30–52 and 8–94%, respectively.

Shorter elution times were obtained using vertical electrokinetic cell (just 6 days, using smaller diameter or shorter-height cells and 0.01 M HNO₃ solution as cathode chamber flow) [60], but it is hard to expect that such procedure could be adapted for *in situ* applications. Nonetheless, removal efficiencies of phenanthrene, *p*-xylene, Cu and Pb were 67, 93, 62 and 35%, respectively.

An interesting twist to the technique was brought up by Ma and co-workers, who used bamboo charcoal as adsorbent, in a bench-scale experiment conducted to investigate the simultaneous removal of 2,4-dichlorophenol and Cd from a sandy loam (artificially spiked), at different periodic polarity reversals [61]. After ca 11 days of operating, about 75% of Cd and 55% of the phenol were removed at intervals of 24 h (about half for intervals of 12 h), at soil pH values ranging from 7.2 to 7.4.

The idea of combining EK process with adsorption was investigated also by Lukman from the King Fahd University of Petroleum and Minerals, who used a locally produced granular-activated carbon from date palmpits in the treatment zones. Natural saline-sodic soil, spiked with contaminant mixture (kerosene, phenol, Cr, Cd, Cu, Zn, Pb and Hg), was submitted to a 21-day period of continuous electrokinetics-adsorption experimental run, the efficiency for the removal of Zn, Pb, Cu, Cd, Cr, Hg, phenol and kerosene being 26.8, 55.8, 41.0, 34.4, 75.9, 92.49, 100.0 and 49.8%, respectively [62]. Lukman also demonstrated the importance of the processing fluids (anolytes and catholytes), which are rapidly degrading depending on the applied voltage gradient, ultimately leading to an eventual rise in the cost of operating the remediation process [63].

A significant improvement was brought to EK process by combining it with ultrasonication. This led to an enhancement of the remediation rate of soils co-contaminated with Pb and phenanthrene [64]. The migration of water and contaminants in the porous soil media is permitted through the actions of electro-osmotic flow and electromigration by electric power and acoustic flow by ultrasonic waves. The accumulated outflow and contaminant-removal rate were higher by the addition of vibration, cavitation and sonication effects. However, if efficiency seemed to improve (the removal rates of Pb and phenanthrene were average 88 and 85% for electrokinetic test and average 91 and 90% for electrokinetic and ultrasonic test, respectively), the duration was not reduced—it still needed ca 15 days of treatment, which means that by using both EK and ultrasonication the costs are higher.

A comprehensive review on the status of *in situ* applicable electrokinetic processes (Electro-Klean™ Electrical Separation, Electrokinetic Bioremediation, Electrochemical GeoOxidation (ECGO), Electrochemical Oxidative Remediation of Groundwater, Electrochemical Ion Exchange (EIX), Electrosorb™ and Lasagna™ process) was presented by E.M. Morales, from PGATech [65].

2.3. Bioremediation processes

Bioremediation generally uses living organisms (usually microbial metabolism), in the presence of optimum environmental conditions and sufficient nutrients, to break down soil organic and inorganic contaminants. Since it represents an attractive method due to the ease of *in situ* applications, bioremediation methods have been reviewed over the past few years, mostly depending on the nature of the polluting agent (heavy metals, PAHs, polychlorinated compounds, pesticides, etc.) or on the contaminated matrix (soil, sediments, groundwater, etc.) [66–70]. Since the method proved effective for both types of contaminants, attempts for simultaneous decontamination did not take long to appear.

A first approach was the so-called ‘bioaugmentation’: metal-contaminated soils were enriched with metal-detoxifying microorganisms while organic-contaminated soils were supplemented with organic-degrading microorganisms [71]. In such of the first examples, a co-contaminated soil with both Cd and 2,4-dichlorophenoxyacetic acid (2,4-D), the degradation of both contaminants was realized by introducing specific microorganisms for each contaminant (*Ralstonia eutropha* JMP134 for 2,4-D and *Arthrobacter*, *Bacillus* and *Pseudomonas* species for Cd) [72]. Contaminated soil with sulphide ore ashes and aromatic hydrocarbons from a historical

industrial site underwent sequential leaching by 0.5 M citrate and microbial treatments [73]. The acidic-leached soil was bioaugmented with *Allescheriella*, *Stachybotrys*, *Phlebia*, *Pleurotus pulmonarius* and *Botryosphaeria rhodina*, which proved to be the most effective, leading to a significant depletion of the most abundant contaminants, including 7-H-benz[*d,e*]anthracene-7-one, 9,10-anthracene dione and dichloroaniline isomers. Simultaneously, the overall metal content was sensibly diminished under the action of *P. pulmonarius*.

The discovery of the dissimilatory metal reduction [74] under the action of heavy metals reducing bacteria provided the idea for the next step. It was soon afterwards that it became clear that the reduction can occur only in the presence of a hydrogen donor, usually water or an organic compound. Thus, Cr(VI)-reducing bacteria may utilize a variety of organic compounds as electron donors for Cr(VI) reduction, though the organic compounds are generally limited to natural aliphatics, mainly low-molecular-weight carbohydrates, amino acids and fatty acids [75]. Thus, why not have the organic pollutant as hydrogen donor, resulting thus in its oxidation? A good hydrogen donor, and also a well-known organic pollutant, is phenol. Indeed, soils co-polluted with a heavy metal such as Cr(VI) and phenol can be decontaminated in the same time by using strains of *P. aeruginosa* [76]. Another strain of *Pseudomonas*, *P. fluorescens*, allowed a drastic reduction of the concentration of heavy metals (Cu^{2+} , Cd^{2+} , Ni^{2+} and Pb^{2+}) but also of phenols and various pesticides (hexachlorobenzene, mancozeb or 2,4-D) in water [77]. Not only *Pseudomonas* strains were able to perform dual Cr(VI) reduction/phenol degradation, but also *Stenotrophomonas* species [78].

Similar examples of metal-reducing bacteria used in dual decontamination procedures are summarized in the following. *Geobacter metallireducens* was successfully used for the biodegradation of toluene and bioleaching of As, and in the same time for an accelerated degradation rate of toluene with reductive dissolution of Fe and co-dissolution of As [79]. In another paper, *Actinobacteria*, in a mixture with some *Streptomyces* spp. *Amycolatopsis tucumanensis*, were used to remediate soil co-contaminated with Cr(VI) and lindane [80]. It is interesting that the incubation period was of only 14 days.

At a certain level, phytoremediation can be considered as a bioremediation [81, 82]. According to the same rationale, if the phytoremediation process can be applied separately to heavy metals [83] and organic pollutants [84, 85], then it can be applied to co-contaminated soils with both species [86]. However, due to its limitations (phytoremediation is applicable only to root-deep soil horizons), there are very few examples of co-decontamination.

One such example is the use of willows for a dual decontamination Cd—oil [87] and another is the use of maize for soil polluted with Cd and pyrene [88].

It is interesting to mention the fact that in a recently published review on the applicability of phytoremediation of soils with mixed organic and heavy metal contaminants, Reddy (*vide supra*) and co-workers identified the most suitable species that proved to be effective separately for heavy metals and organic contaminants, but that were never investigated in simultaneous phytoremediation.

An alternate route was taken by an Italian team led by Baldi, from the Ca Foscari University of Venice, consisting of a first step of bioprecipitation followed by fungal degradation of organic

pollutants from contaminated soils [89]. Thus, the contaminated soil was leached with 0.5 M citric acid leading to a good removal of metals and a low removal of organic contaminants (12%). The leachate was then incubated with a metal-resistant *Klebsiella oxytoca* strain, capable of using residual citrate to produce an iron gel that co-precipitated metals. In the same time, the leached solid waste was bioaugmented with a fungus strain of *Allescheriella* to complete the degradation of several organic contaminants, including trichlorobenzene, naphthalene, dichloroaniline and pentachloroaniline.

2.4. Miscellaneous processes

In this area, there are two possibilities: processes that combine aspects of the above procedures (washing, EK and bioremediation) or processes that are completely different, belonging to the immobilization/sorption techniques or to the purely chemical or thermal types of technologies.

Thus, either washing or electrokinetic process can be improved if realized with the augmentation of the naturally occurring microbial activity. In a recent report, PAHs and heavy metal-polluted soil from an abandoned coking plant was in a first step cleaned up by using a methyl- β -cyclodextrin solution to enhance ex situ extraction of PAHs and metals simultaneously, followed by the addition of PAH-degrading bacteria (*Paracoccus* sp. strain) and supplemental nutrients to treat the residual soil-bound PAHs [90]. Elevated temperature (50°C) in combination with ultrasonication was also needed. In the second case, the authors studied the benefits of integrating electrokinetic remediation with biodegradation for decontaminating soil co-contaminated with crude oil and Pb, in laboratory-scale experiments lasting for 30 days [91].

Immobilization techniques imply the adsorption of both heavy metals and organic contaminants on a solid support, usually biochar [92]. Cao et al. demonstrated that incubated biochar (prepared from dairy manure) for 210 days was effective for immobilization of both atrazine and Pb (its effectiveness was enhanced by increasing incubation time and quantity) [93]. After treatment, soils to which ca 5.0% biochar was added showed more than 57 and 66% reduction in Pb and atrazine concentrations, respectively.

On the chemical side of dual degradation processes, there are mentions of some techniques that use a photochemical activation. The problem encountered by photocatalytic processes is that they need the *a priori* formation of a solution. Thus, in an aqueous solution, it was possible to simultaneously reduce Cr(VI) and oxidize benzoic acid, in a suspension of N-F-co-doped TiO₂ [94]. Therefore, photocatalytic process must follow a washing step [95].

In a purely chemical process, Mitoma and co-workers used a nano-size mixture of metallic Ca and CaO that played a double role: in combination with a hydrogen donor (naturally occurring moisture) can hydrodechlorinate harmful dioxin compounds and during mixing can immobilize heavy metals in a cement-like matrix [96]. Thus, a soil contaminated with both heavy metals and dioxins (the most common type of polluted soil from reclaimed factories) can be safely treated.

The thermal type of co-decontamination process is illustrated by only one example, in which PCDD/Fs, pentachlorophenol and mercury are simultaneously removed [97]. This is under-

standable since other than Hg, all the other heavy metals are thermally quite stable (Hg has a boiling point of 356.73°C).

3. Conclusion

The multiplication and diversification of the methods for simultaneous decontamination of soils co-contaminated with both heavy metals and organic pollutants represent a certainty for a more rapid cleansing of polluted soils, associated with lower costs and more environmentally friendly procedures. Thus, physical/chemical, biological and thermal methods are combined in order to offer a wide variety of procedures that allow an effective removal or immobilization of various classes of pollutants. Therefore, after profiling the pollutants composition of a particularly heavy polluted soil, one has now a large choice of methods for treatment in order to simultaneously remove two or even several pollutants in a single batch. These methods are ranging from simple washing to electrokinetic or biological procedures; others include combinations of the previous or even thermal or purely chemical methods. Choosing one or another of these methods will depend on the type of pollutants and the ratio costs/effectiveness. Nevertheless, any of these methods can allow an effective treatment with lower cost and duration than those necessary in effective but separate treatments for each pollutant.

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