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MONITORING AND REMEDIATION OF HEAVY METAL POLLUTED SOILS – A REVIEW

Summary

Soil contamination by heavy metals poses a threat to plants, terrestrial animals, and in consequence, human health. Heavy metals emitted primarily by anthropogenic activity may be accumulated in edible plant or animal tissues and then consumed by humans. The need for a reliable detection and continuous monitoring of heavy metal contents in agricultural soils is undeniable. Moreover, a cost-effective and environmental friendly remediation methods are required for and efficient mobilization or immobilization of the metal in soil. This paper reviews two promising in situ monitoring methods (Vis-NIR/MIR and PXRF) and four remediation methods (physical/chemical remediation, animal remediation, phytoremediation and bioremediation) that could be used in order to improve the quality of heavy metal polluted soils.
Key words: *heavy metals, soil, Vis-NIR, MIR, PXRF, phytoremediation, bioremediation*

MONITORING ORAZ REMEDIACJA GLEB ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI – PRZEGLĄD STOSOWANYCH ROZWIĄZAŃ

Streszczenie

Zanieczyszczenie gleb metalami ciężkimi stanowi poważne zagrożenie dla roślin, zwierząt glebowych oraz, w konsekwencji, dla ludzkiego zdrowia. Metale ciężkie, emitowane głównie w wyniku ludzkiej aktywności, mogą akumulować się w jadalnych częściach roślin oraz w mięsie zwierząt hodowlanych, spożywanych następnie przez ludzi. Potrzeba wiarygodnej detekcji oraz stałego monitoringu metali ciężkich w glebach uprawnych jest niepodważalna. Ponadto, niezbędne jest zastosowanie taniej oraz przyjaznej środowisku metody remediacji zanieczyszczonych obszarów, celem zwiększenia lub zmniejszenia mobilności metalu w glebie. Ta praca przeglądowa skupia się na analizie dwóch obiecujących metod monitoringowych (Vis-NIR/MIR oraz PXRF) oraz czterech metod remediacyjnych (remediacji fizycznej/chemicznej, remediacji przy użyciu zwierząt, fitoremediacji oraz bioremediacji), które mogą zostać użyte w odniesieniu do gleb zanieczyszczonych metalami ciężkimi.
Słowa kluczowe: *metale ciężkie, gleba, Vis-NIR, MIR, PXRF, fitoremediacja, bioremediacja*

1. Introduction

Due to an intensive urbanization, mining, rapidly developing industry and irresponsible agricultural processes, the number of contaminated soil sites across the globe reached the value of 10^7. In the European Union there are about 342 000 of contaminated sites and 2.5 million of potentially contaminated sites [1]. However, in Europe only about 5% of the contaminated and potentially contaminated soils were subjected to some kind of remediation [2]. The remediation of polluted soils depends on various factors including the type of contaminant and the amount of contaminated soil. In the environment soil plays important role as a natural habitat for many terrestrial organism, provides fundamental resources for the survival of plants and other organism, but also due to its filtering and buffering properties can be treated as a natural sink accumulating many of the pollutants. The soil is regarded as "contaminated" when the concentration of a particular contaminant is above a defined background value and may cause a risk to terrestrial organisms and human health through the food chains [3].

Heavy metals are the contaminants widely found in many polluted soils across the globe. The term "heavy metals" includes chemical elements (both metals and metalloids) with atomic density greater than 6 g cm^{-3} [4]. Among them one can differ two groups – biologically essential [e.g., cobalt (Co), copper (Cu), chromium (Cr), manganese (Mn) and zinc (Zn)] and non-essential [e.g., cadmium (Cd), lead (Pb) and mercury (Hg)] elements. The essential elements (in low concentrations) are vital for life for plants, animals and humans. On the other hand, non-essential elements are redundant for living organisms. However, both heavy metal groups are toxic to terrestrial organisms and humans in high concentrations [5]. The sources of heavy metals in soils can be both geogenic and anthropogenic. Most of the metals occur in natural materials including igneous and sedimentary rocks, but also coal. Moreover, volcanic eruptions generating tons of dusts are one of the major sources of heavy metal emission into the atmosphere (and then to water or soil). However, anthropogenic activity, mainly associated with coal power plants, glass and metal smelters and other industrial processes, is a major source of metals found in the environment. For instance, pollution of soils by Pb originating from a leaded-gasoline was a major concern in many countries for many years [6]. One of the main problems in agriculture concerns P (phosphorus) fertilizers containing significant amounts of Cd. Cadmium in such fertilizers originates from phosphate rocks used for manufacturing of the fertilizer [7]. Moreover, a continuous use of Cu-based fungicides and the use of Cu in horticulture (growth promoters used for piggery and poultry) poses a threat to humans due to bioaccumulation of Cu in edible plants and livestock meat [8, 9].

Unlike organic pollutants, such as petroleum hydrocarbons and chlorophenols, heavy metals do not undergo microbial or chemical degradation and can persist in soil for a long period of time [7]. However, only limited amount of the metal is available to living organism, as the weathering/aging processes, water-soil distribution of metal, speciation of metal in soil solution and absorption of metal by living organism determine the final toxicity towards terrestrial organisms [10]. Nevertheless, heavy metals are accumulated by plants, which are consumed by herbivores. Therefore, high metal contents can be found in plant and animal tissues consumed by humans. Heavy metals accumulated in human body disrupt the function of vital organs such as heart, brain, kidneys, bone and liver. Moreover, a chronic exposure to low doses of heavy metals may induce different kinds of cancer [11].

Considering the fact that heavy metals are widely found in the environment and pose a threat to human health, there is a need of technology to clean up the soil sites polluted by heavy metals and monitor their contents in time. The technologies should not only be feasible, efficient, environmental friendly, but also cost-effective. The aim of this study was to present a range of technologies used both in monitoring and remediation of heavy metal polluted soils.

2. Monitoring of heavy metal polluted soils

The knowledge about the true content of metal in soil is essential in terms of selection of a proper remediation technique. Conventional methods used in laboratory involve time-consuming sample preparations and are no longer attractive for *in situ* (in the field) monitoring of heavy metal content in contaminated sites. However, there are two fast and novel methods that could be used to estimate the heavy metal contents in soil: (i) infrared reflectance spectroscopy, and (ii) X-ray fluorescence.

2.1. Infrared reflectance spectroscopy (Vis-NIR and MIR)

Compared to conventional "wet chemistry" methods (e.g. atomic absorption spectroscopy – AAS), visible and near-infrared (Vis-NIR, wavelength: 400 – 2500 nm) spectroscopy and mid-infrared (MIR, wavelength: 2500 – 25 000 nm) spectroscopy are non-destructive and cost-effective techniques. These methods do not require a large volumes of hazardous chemical reagents and are fast and repeatable. Moreover, both techniques could be used not only in a laboratory conditions, but also directly in the contaminated site [12]. Finally, MIR could be also used for simultaneous estimation of petroleum hydrocarbons contents in soil. Absorption spectra obtained by using Vis-NIR or MIR are a reflection of molecular structures of chemicals that could be found in soil. The absorption of particular chemical compounds is a consequence of a vibrational energy transitions of dominant molecular bonds. The absorption over Vis-NIR spectral regions is primarily associated with the presence of Fe-oxides, clay minerals, organic matter and water [1].

Some heavy metals (i.e. Ni, Cu, Co, and Cr) also exhibit absorption features in the visible/near-infrared regions. However, detection limit for such metals is high, since their minimal content in soil should exceed 4000 mg kg^{-1} [13]. Mentioned high heavy metal contents could be only found in mining and industrial areas. Although heavy metals occurring in soil in low or moderate concentrations could not be directly detected using Vis-NIR, they bound to Fe-oxides, clays and organic matter and may influence the absorption spectra of such soil components [3]. As a result of the interactions between heavy metals and mentioned soil constituents, the content of heavy metals in soil could be estimated using reflectance spectra of soil [14]. This indirect way of assessing metal content in soils is possible due to empirical mathematical models, which associate content of a particular metal with content of either Fe-oxides, clays or soil organic matter [15, 16]. However, this estimation may be location-based, and thus, different for different sites across the globe [3]. Both Vis-NIR and MIR techniques could be easily used in the field, as the portable spectroradiometers are commercially available. The use of infrared spectroscopy has limitations, since the soil surface and atmospheric conditions have a significant influence on the results [17]. For instance, the reflectance decreases as the moisture of soil increases. However, these issues could be mitigated, as the field spectra provide inexpensive data for exploring of the possible solutions. Although the use of space-borne hyperspectral imaging spectrometers, which could monitor larger contaminated areas, is currently too expensive, it may become available in the future with the launch of satellites with high spectral resolution sensors [18].

2.2. Portable X-ray fluorescence (PXRF)

Similarly to Vis-NIR and MIR, portable X-ray fluorescence (PXRF) has been recognized as a useful way of measuring heavy metal contents in soil. PXRF enables fast, real-time and simultaneous multi-elemental detection of soil samples and requires no or small chemical treatment. The principles of the method are as follows: electrons leave their energy shells when excited with X-rays and their vacant positions are then filled with other electrons from higher energy shell, which results in an emission of a X-ray fluorescence photon with wavelength characteristic for each atom [19].

Detection limit of PXRF devices enables a reliable measurement of significant contents of metals/elements (As, Ba, Cd, Co, Cr, Cu, Hg Mo, Ni, Pb, Sn, V and Zn). During recent years the accuracy of PXRF devices has increased and now detection limits for heavy metals are smaller than 10 mg kg^{-1}. Thus, the accuracy of PXRF technique is similar to widely used, laboratory-based AAS [20]. The final accuracy of the device, however, depends on physical matrix effects related to the soil particle size, surface irregularities and soil moisture [1]. Therefore, dry conditions and proper homogenization of soil are recommended for accurate detection of chemical elements using PXRF. Chemical matrix effects are another aspect that should be considered, since some chemical elements can absorb or enhance X-rays. For instance, X-ray intensities for Zn are absorbed in the presence of high contents of Fe. However, most of the effect could be mitigated and corrected by PXRF software [21]. Generally, a sample pretreatments including drying and sieving are required to accurately quantify the content of heavy metal in soil. The PXRF spectrometers are widely available and could be easily used *in situ*. In this case, device is either placed directly onto soil surface or could scan soil through plastic bags [1]. The PXRF devices were successfully used in the field for monitoring of metal contents in soil [22, 23]. In summary, PXRF is a promising method to be used as a rapid in-field analytical technique. However, the regulatory limits of some of the metals may not fall above the limit of detection and this issue should be taken into consideration during selection of the method.

3. Remediation of heavy metal polluted soils

Most of the remediation methods dedicated to heavy metals can be divided into two categories: (i) methods that immobilize metal in soil and make it less available to living organisms, and (ii) methods that mobilize metal in soil and enable it removal from the soil. There are numerous processes that can be used to mobilize or immobilize heavy metal in soil matrix. Firstly, metals may be retained in soil as a result of sorption, precipitation or complexation reaction. On the other hand, they may be removed from the soil by leaching, plant uptake or (in some cases) volatilization [7]. To date, four major remediation methods were considered as efficient in remediation of heavy metal polluted soils: (i) physical/chemical remediation, (ii) animal remediation, (iii) phytoremediation, and (iv) bioremediation.

3.1. Physical/chemical remediation

Physical remediation incorporates soil leaching or absorbent fixation. The aim of the first technique is to mobilize the metal and then wash it out from the soil matrix e.g. using pure water or water solutions. On the other hand, fixation of the metal by using an absorbent enables a stronger immobilization of the metal to make it less bioavailable to living organisms. Chemical remediation is mainly associated with the addition of synthetic chelating reagents such as EDTA (ethylenediaminetetraacetic acid). Chelating agents increase both solubility and bioavailability of the metal, and thus, its concentration in soil solution [24]. However, most of the used synthetic chelating agents are considered as pollutants and their use in remediation is questionable. On the other hand, synthetic chelating reagents could be not selective and chelate the metals which are in greater amount in the soil (e.g. Fe or Ca) [25]. Therefore, methods which incorporate animals, plants and microorganisms are preferred, since they are more cost-effective and environmental friendly.

3.2. Animal remediation

The animals that are used in remediation of heavy metal polluted soils are earthworms. This group of organisms plays important role in the soil environment and improve soil quality [26]. Earthworms produce organic material with attached –COOH and –CO chemical groups, which acidify soil and mobilize heavy metals in soil. However, due to small amount of earthworms that can be introduced to the contaminated soil, the efficiency of this method is still limited. Moreover, the final results of this kind of remediation depends on outer conditions (e.g. pH of the contaminated soil) [27].

3.3. Phytoremediation

The use of plants in remediation is one of the most promising methods to remove, transfer and stabilize heavy metals from contaminated soils. The phytoaccumulator plants are widely used in removal of metals from the soil. Heavy metals are in this case accumulated in plant shoots and after harvesting of the plant can be transferred to another, protected place. This kind of phytoremediation is often named phytoextraction. The roots of plants have the ability to exert protons to surrounding soil, which acidify the soil and improve the mobility of the metals [28]. Moreover, the presence of transporter proteins, exerted natural chelators (e.g. phytochelatin) and natural organic acids mitigate the transport of the metals into cells [25]. The phytoaccumulator plants protect themselves from toxic impact of accumulated metals, since the accumulation is usually located in vacuoles, which have the ability to control the distribution and concentration of the metal within the cell [29]. Some metals such as Hg are removed from the plant by converting toxic metal into less toxic volatile form. Compared to conventional physical/chemical techniques, the cost of phytoextraction is about 10 times lower per hectare [30]. *Brassica napus* was selected as major plant for accumulating Cd and Pb. On the other hand, *Andrographis paniculata* is better solution for co-removal of Zn and Cd from contaminated soil [31, 32]. Plants can be also used to reduce the mobility of heavy metals in soil. This technique also known as phytostabilization enhances the absorption and precipitation of metals. Recent studies have demonstrated that intensive penetration of roots into the soil, reduced leaching and immobilized heavy metals in the roots surroundings [33].

3.4. Bioremediation

Bioremediation is a remediation technique that uses a potential of microorganisms to clean up the environment. Some of the microorganism demonstrate ability to exert special redox enzymes that change the oxidation state of the metal. This conversion may result in a transformation of the metal into less toxic state. For instance, the reduction of Cr(VI) to Cr(III) ensure the decrease in toxicity and mobility of the metal [25]. The second example of this mechanism is a conversion of methylmercury into Hg(II) (which is about 100 times less toxic) by mercury-resistant bacteria able to produce organomercurial lyase (MerB) [34]. Metals can be also immobilized by an extracellular mixture of polysaccharides, mucopolysaccarides and proteins produced by microorganisms [35].

The combined technique of phytoremediation and bioremediation is an excellent solution for an improvement of heavy metal removal from soil. Symbiotic bacteria inhabiting rhizosphere provide better acidification of the soil, which leads to better solubility of heavy metals and their higher bioavailability to plant roots. Next, heavy metals can be absorbed by the roots, transported in the xylem, detoxified (through chelation, vacuolar compartmentalization or volatilization) and accumulated in the vacuoles. The efficiency of this hybrid-technique is usually higher compared to phytoremediation and bioremediation considered separately [25].

4. Conclusions

Since the contamination of the soils by heavy metals poses a serious threat to the environment and human health, there is a need for a reliable detection and monitoring methods – especially in the case of agricultural soils. Two of the most promising monitoring methods include Vis-NIR/MIR and PXRF. However, not only continuous monitoring of the soil contamination is necessary, but also an efficient method of its remediation. Due to the fact that metals do not undergo natural degradation in time, the mobilization (and then leaching) or immobilization (decreasing of the bioavailability) of the metal should be applied. In this case, phytoremediation and bioremediation, which can be applied either separately or simultaneously are the most cost-effective, environmental friendly, and thus, promising methods.

5. References

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