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Review

Natural carriers in bioremediation: A review

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A R T I C L E I N F O

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A B S T R A C T

Bioremediation of contaminated groundwater or soil is currently the cheapest and the least harmful method of removing xenobiotics from the environment. Immobilization of microorganisms capable of degrading specific contaminants significantly promotes bioremediation processes, reduces their costs, and also allows for the multiple use of biocatalysts. Among the developed methods of immobilization, adsorption on the surface is the most common method in bioremediation, due to the simplicity of the procedure and its non-toxicity. The choice of carrier is an essential element for successful bioremediation. It is also important to consider the type of process (*in situ* or *ex situ*), type of pollution, and properties of immobilized microorganisms. For these reasons, the article summarizes recent scientific reports about the use of natural carriers in bioremediation, including efficiency, the impact of the carrier on microorganisms and contamination, and the nature of the conducted research.

Contents

1. Introduction

The twentieth century went down in history as a period of extremely dynamic civilizational and technological development. Industrialization, wars, and intensive use of large-scale heavy metals and synthetic xenobiotics led to many environmental problems [1,2].

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The contamination of the environment by petroleum products, pharmaceutical compounds, chloro- and nitrophenols and their derivatives, polycyclic aromatic hydrocarbons, organic dyes, pesticides and heavy metals is a serious problem [3,4,5,6,7,8,9]. These pollutants enter the environment by different ways. For example, one of the major consequences of the armed conflict between Iraq and Kuwait was the release into the environment millions of barrels of crude oil. After the war ended, scientists began numerous studies aimed at the removal of oil from the contaminated environment. Other sources of crude oil in ecosystems are accidental oil spills. One of the biggest marine disasters took place in Mexico in 2010, and it resulted in the spewing out of about 2.8 million barrels of crude oil from the British Petroleum (BP) oil rig Deepwater Horizon into the sea [10,11].

Pesticides are other serious pollutants present in soils. USEPA reported that in 2007, global consumption of pesticides for agricultural purposes was 2.36 million tonnes [12]. These compounds, used in bulk for long periods of time in a limited area, lead to serious disorders in indigenous microflora and humans, because pesticides are also toxic to non-target organisms [12,13,14]. Moreover, many metabolites of pesticide biodegradation are also toxic and constitute priority pollutants. For example, the major metabolites of parathion and 2,4-dichloropenoxy acetic acid biodegradation are *p*-nitrophenol and 2,4-dichlorophenol, respectively [9,15,16,17,18].

It has been reported that many microorganisms are able to biodegrade different pollutants [4,5,7,8,19,20]. However, the biodegradation rate depends on the physiological state of the microorganisms, which are sensitive to variable environmental factors. It is known that immobilization improves microorganisms' resistance to unfavourable environmental impacts [6,8].

The main purpose of this review is to present and discuss the latest reports about the natural carriers in the processes of bioremediation by immobilized cells. In the article immobilization methods for bioremediation are also presented.

2. Bioremediation methods

In 1930 Tausz and Donath [21] presented the idea of using microorganism to clean soil contaminated with petroleum derivatives, giving rise to biodegradation processes. Today, bioremediation is a commonly used method to restore the natural and useful values of contaminated sites by microorganism able to degrade, transform, or chelate various toxic compounds [22]. Microorganisms can break down organic pollutants by using them as a source of carbon and energy, or by cometabolism. Heavy metals cannot be degraded or destroyed biologically and undergo transformation from one oxidative state or organic complex to another. It changes their water solubility and decreases their toxicity [22,23].

Bioremediation is eco-friendly, non-invasive, cheaper than conventional methods, and it is a permanent solution that can end with degradation or transformation of environmental contaminants into harmless or less toxic forms [23,24,25,26]. Soil bioremediation can be carried out at the place of contamination (*in situ*), or in a specially prepared place (*ex situ*). *In situ* technology is used when there is no possibility to transfer polluted soil, for example when contamination affects an extensive area [26,27,28].

There are three basic methods of *in situ* bioremediation with microorganisms: natural attenuation, biostimulation, and bioaugmentation [24,29,30].

Natural attenuation is connected with the degradation activities of indigenous microorganisms. This method avoids damaging the habitat, allows ecosystem revert to its original condition and enables detoxification of toxic compounds [24,31].

Removal of contaminations by the natural attenuation takes a long time because degrading microorganisms in soil represent only about 10% of the total population. The increase of bioremediation efficiency *in situ* may be realized in the bioaugmentation process, in which the specific degraders are introduced into the soil [30,31]. This method is applied when the indigenous microflora are unable to break down pollutants, or when the population of microorganisms capable of degrading contaminants is not sufficiently large. To make the process of bioaugmentation successful, microorganisms introduced into the polluted environment as a free or immobilized inoculum should be able to degrade specific contamination and survive in a foreign and unfriendly habitat, be genetically stable and viable, and move through the pores in the soil. Microorganisms can be previously isolated from the contaminated soil and propagated, or their functional ability can be enhanced in the laboratory. Nonindigenous strains or genetically modified microorganisms (GMM) can also be incorporated into the remediated soil [31,32,33,34]. However, the result of bioaugmentation depends on the interaction between exogenous and indigenous population of microorganisms because of the competition, mainly for nutrients [31].

To accelerate *in situ* bioremediation processes, biostimulation is used in order to modify the physical and chemical parameters of the soil. For this purpose, compounds such as nutrients (*e.g.* biogas slurry, manure, spent mushroom compost, rice straw and corncob) or electron acceptors (phosphorus, nitrogen, oxygen, carbon) are introduced into the soil [29,30,32,35].

Because *in situ* processes are out of hand it is difficult to predict the effect of remediation of contaminated sites [28]. *Ex situ* methods allow more efficient removal of pollutants, by controlling the physico-chemical parameters, resulting in a shortening of the total time of reclamation. These advantages outweigh *ex situ* methods' disadvantages such as additional cost and risk connected with the possibility of dispersion of the contamination during transport. During the *ex situ* processes contaminated media is excavated or extracted and moved to the process location. Liquids can be clean in constructed wetlands while semi-solid or solid wastes in slurry bioreactors. Solid contaminations are biodegraded through land farming, composting and biopiles [26,28,36,37].

Constructed wetlands are used with success in the treatment of wastewater derived from domestic, industrial or agricultural sources [38]. They require the competition of microbes (bioremediation) and plant (phytoremediation). Microorganisms degrade or sorb organic substance present in the water undergoing treatment. Plants are used to remove, transfer or stabilize contaminants through metabolism, accumulation, phytoextraction or immobilization at interface of roots and soil [37]. Bioremediation processes in slurry bioreactors can be performed under aerobic or anaerobic conditions [28]. These systems utilize naturally occurring microorganisms or strains possessing specific metabolic capabilities to transform toxic compounds [27]. Slurry bioreactors are one of the best applied technologies used in the bioremediation of contaminated soils because they undergo under controlled operating conditions. It allows for the enhancement of microorganisms activity [27,39,40].

Landfarming is one of the most widely used soil bioremediation technologies. In this technology, excavated contaminated soils are spread out in a thin layer on the ground surface. Aerobic microbial activity within the soil is stimulated through the aeration and addition of minerals, nutrients and moisture [41,42]. Landfarming is a relatively simple technology however it is inexpensive and effective for easily biodegradable contaminants only at low concentration [28,37,41,42,43]. Composting is a controlled biological process that treats of agricultural and municipal solid wastes and sewage sludge using microorganisms under thermophilic and aerobic conditions [28,37]. Through composting, it is possible to reduce the volume of residues in landfills. Biodegradation of solid contaminants takes place mainly as a result of oxidation and hydrolysis. The optimum temperature for growth of microorganisms engaged in composting is in the range of 40 to 70°C. The risk of contamination by pathogens is small, because most of them are inactivated at 70°C. A key factor during composting is microbial accessibility to the pollutants and the characteristics of the amending