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International Biodeterioration & Biodegradation 58 (2006) 248–253

INTERNATIONAL
BIODETERIORATION &
BIODEGRADATION

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Potential use of organomineral complex (OMC) for bioremediation of pentachlorophenol (PCP) in soil

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Received 30 May 2005; received in revised form 13 February 2006; accepted 14 June 2006

Abstract

Adsorption/desorption characteristics for the organic pollutant pentachlorophenol (PCP) were determined for the organomineral complex (OMC) prepared in the laboratory with clay mineral (zeolite–clinoptilolite) and organic matter (humic acids), both natural products with excellent sorption properties. Sorption experiments were carried out in three characterized soil samples, Calcaro-haplic Chernozem, Gleyic Fluvisol, and Arenic Regosol. The results of this study indicate that OMC has better retention abilities than the clay minerals alone. Higher amounts of humic acids (HAs), bound to zeolite, enhance its potential to adsorb and retain PCP. An OMC containing approx. 5 mg HA g^{-1} of zeolite possessed the best retention ability for PCP and presented an optimal economic solution from the preparation point of view. Then biodegradation of PCP was studied in the same types of sterilized soils bioaugmented with the bacterial isolate *Comamonas testosteroni* CCM 7350, with and without the addition of OMC. The immobilization effect of OMC in relation to PCP depends on the concentration of PCP and the content of organic carbon in the soil. The activity of the microorganisms and the effect of acid rain led to the gradual release and biodegradation of the irreversibly bound PCP, without any initial toxic effect on indigenous or bioaugmented microorganisms. OMC appeared to be a good adsorbant for PCP, with potential application in remediation technology. Fast and effective adsorption and low desorption may serve as a pretreatment step for bioremediation technology for reducing PCP content in soil and thus for reducing its potential toxicity, reducing bioavailability, and in this way facilitating biodegradation.

Keywords: Bioremediation; Humic acids; Organomineral complex; Pentachlorophenol; PCP; Sorption; Zeolite

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1. Introduction

Immobilization processes in soil are of great environmental importance, as they may lead to a considerable reduction in the bioavailability and, as a result, of the toxicity of xenobiotics such as pesticides (Hatzinger and Alexander, 1995). The ability of soil to retain organic contaminants is attributed to adsorption phenomena and chemical reactions that occur on active surfaces of humic substances and mineral particles. Some xenobiotics can also be retained through entrapment within the soil matrix (Calderbank, 1989; Bollag et al., 1997). The incorporation of xenobiotic organics and their derivates into soil organic matter occurs readily in nature. This process can be used to immobilize and detoxify hazardous compounds. The immobilization phenomena have several important consequences: (1) the amount of compound available to interact with biota is reduced; decreased bioavailability can lead to reduced toxicity, (2) the complexed products are less toxic than their parent compounds and (3) binding restricts leaching of chemicals through the soil profile, thus preventing groundwater contamination. Neither laboratory research, nor practical observations, demonstrated

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doi:10.1016/j.ibiod.2006.06.017

any significant negative or toxic impact of bound xenobiotics on the environment; hence the immobilization of pollutants in soil has been recognized as a promising decontamination technique (Bollag, 2002).

It is important to monitor binding of contaminants to organic matter, as this can reduce bioavailability to degrading microorganisms. This may lead to a false conclusion about the microbial contribution to degradation. On the other hand, it is possible to use the sorption properties of contaminant to the benefit of microorganisms. High influent concentrations can be decreased to less toxic levels by adsorption to allow maximum degradation to take place.

The key role in elimination of contaminants from the soil is played by the quality of organic matter and mainly by humic acids (HAs). HAs are very active in interactions with organic and inorganic contaminants. Their excellent sorption properties depend on their chemical structure and composition. HAs isolated from different matrices (soils, lignite) have different sorption capacities with regard to binding of heavy metals and organic contaminants. Our previous study confirmed that the origin and age of soil and lignite matrices have considerable effect on the structure and properties of isolated HAs (Barančíková et al., 2003). According to the literature, coal and lignite HAs usually contain more aromatic compounds (Lawson and Stewart, 1989). Naumova et al. (2002) suggested that the higher detoxification activity of coal HAs in comparison with soil HAs can be explained by the higher content of aromatic compounds. Lignite HAs contain a 20-fold higher content of organic carbon than does agricultural soil.

The role of microorganisms in these processes is to condition the xenobiotic molecules for covalent binding (Sarkar et al., 1988). Experiments using ^{14}C-labeled compounds demonstrated that generally only negligible amounts of bound residues were formed in sterile soil. Microorganisms can also partially degrade xenobiotics, thus converting them to more reactive derivatives that may be involved in subsequent covalent binding. As a result of binding, however, these derivatives are resistant to further degradation or mineralization on exposure to microbial populations. Xenobiotic phenols were assumed to form covalent linkages with soil organic matter (Agathos and Reineke, 2002; Dec and Bollag, 1988). They first had to be enzymatically oxidized to aryloxy free radicals or quinones to become bound to humic substances. Phenols are precursors of HAs, being a part of their structure (Bollag et al., 1980; Bollag, 1992).

Before binding of xenobiotics to humus can be applied as a decontamination procedure, the stability of the bound complexes must be investigated. If large quantities of a bound pollutant were to be released in the future, the accumulation of these complexes would pose a delayed environmental hazard (Bollag, 2002). Biological and physico-chemical factors, the activity of microorganisms, and acid rain are believed to be the primary factors responsible for the release of bound residues. Overall, the available data indicate that the microbial release of bound xenobiotics occurs at an extremely slow rate. Once released, the xenobiotics can be mineralized or reincorporated into humus. Consequently, released residues are not expected to accumulate and should not pose a delayed health hazard.

Our work was focused on immobilization of pentachlorophenol (PCP) in organomineral complex (OMC) particles. OMC were prepared by binding HAs onto zeolite at laboratory conditions and adding to soil. OMC use excellent sorption properties of both components. PCP represents a widespread environmental concern because of its toxicity and recalcitrance (Dercová et al., 2004). As a consequence of intensive use, it has become a widespread contaminant in soil, sediments, and groundwater. It was mainly used as pesticide, insecticide, and wood preservative, as well as an inhibitor in cooling towers, adhesives, construction materials, paint, and paper. The objective of this work was to provide a study of sorption characteristics of PCP in soil, in soil mixed with zeolite, and in soil mixed with OMC (zeolite and HAs), as well as to examine the biodegradation of PCP in soil with and without OMC.

2. Materials and methods

2.1. Characteristics of soil and lignite HAs

HAs were characterized by CHN elemental analysis, by determination of carboxylic groups, and by ^{13}C NMR spectra, which determine percentage content of aliphatic (C_{alif}) and aromatic (C_{ar}) carbon and degree of aromaticity α.

2.2. Preparation of OMC

HAs were dissolved in 0.01 M NaOH at 5, 25, 50, 100, 200, 500, 1000, and 2000 mg l^{-1}. Fifty milliliters HA was added to 10 g zeolite. The blank was mineral mixed with 0.01 N NaOH. The suspension was mixed for 12 h at laboratory temperature. Solid phase (OMC) was centrifuged, washed with distilled water, and dried at 50 °C.

2.3. Adsorption of PCP onto OMC and soil

A mixture of soil and OMC was prepared. OMC was added to soil at 5% w/w. An adsorption experiment was performed in a 2-g mixture of OMC and soil. The mixture was placed into a 100-ml Erlenmeyer flask fitted with a ground stopper, 50 ml distilled water was added, and a solution of PCP in dimethyl sulfoxide (DMSO) was admixed so that the resulting concentration of PCP was 10 mg l^{-1}. The samples were placed on a rotary shaker (180 rpm) at 28 °C for 1 h. The solid phase was removed by centrifugation (15 min at 5000 rpm); supernatant was decanted, extracted, and analyzed.

2.4. Desorption of PCP from OMC and soil

Upon termination of the adsorption experiment and centrifugation, sediment was quantitatively transferred into a 100-ml Erlenmeyer flask fitted with a ground stopper. About 0.5 g Silipor was carried on the glass filter. The pH value of the sediment was adjusted to 2.5 (simulation of acid rain) and it was placed on a rotary shaker (180 rpm) at 28 °C for 24 h.