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Enhancing agents for phytoremediation of soil contaminated by cyanophos

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ABSTRACT

Cyanophos is commonly used in Egypt to control various agricultural and horticultural pests. It is a strong contaminant in the crop culturing environments because it is highly persistent and accumulates in the soil. This contaminant can be removed by phytoremediation, which is the use of plants to clean-up pollutants. Here we tested several several strategies to improve the effectiveness of this technology, which involved various techniques to solubilize contaminants. The phytoremediation efficiency of *Plantago major* L. was improved more by liquid silicon dioxide (SiO_2) than by other solubility-enhancing agents, resulting in the removal of significant amounts of cyanophos from contaminated soil. Liquid SiO_2 increased the capacity of *P. major* L. to remove cyanophos from soil by 45.9% to 74.05%. In *P. major* L. with liquid SiO_2, leaves extracted more cyanophos (32.99 μg/g) than roots (13.33 μg/g) over 3 days. The use of solubilization agents such as surfactants, hydroxypropyl-ß-cyclodextrin (HPßCD), natural humic acid acid (HA), and Tween 80 resulted in the removal of 60 convergents of cyanophos from polluted soil. Although a batch equilibrium technique showed that use of HPßCD resulted in the efficient removal of cyanophos from soil, a greater amount of cyanophos was removed by *P. major* L. with SiO_2. Moreover, a large amount of cyanophos was removed from soil by rice bran. This study indicates that SiO_2 can improve the efficiency of phytoremediation of cyanophos.

1. Introduction

Cyanophos [O-(4-cyanophenyl) O, O-dimethylothioate] is an organophosphate insecticide with the commercial name of Cyanox that is used to effectively control Aphididae, Coccidae, Diaspididae, Lepidoptera, and other insects on various fruits and vegetables (Tomlin, 2004). Mobile ground spraying with cyanophos for controling quelea, as routinely practiced in Senegal during the 1995/1996 cropping season, was found to be hazardous to the environment (Mullie et al., 1999). Cyanophos is not easily hydrolyzed, and thus it is highly persistent and accumulates in various aquatic compartments such as rivers and lakes (Floesser-Mueller, Swack, 2001). Desmethylcyanophos, 4-Cyanophenol and desmethyl-cyanophos oxon are degradation products of cyanophos in soil (Chiba et al., 1976).

Phytoremediation is a strategy that uses plants to degrade, stabilize and remove contaminants from soils, water and wastes (Yu and Gu, 2008). Phytoremediation is an environmentally sound technology for pollution prevention, control and remediation. Combining plants with solubility enhancement agents such as surfactants, may improve phytoremediation strategies. These techniques are based on the ability of the agents to increase the water solubility of hydrophobic organic compounds (HOCs) – through micellization and surface tension reduction (Saichek and Reddy, 2004) and to promote desorption, bio-degradation and phytoremediation processes (Gao et al. 2007; Wang and Keller, 2009). Different classes of surfactants are employed for soil remediation, depending on the nature of the contaminants. Synthetic surfactants, such as Tween 80, are reported to remove organic pollutants from contaminated soils by a mechanism involving repartition of pollutants into the surfactant micellar phases formed in water. However, this process can take place only when the surfactant solution reaches the surface of the soil particles and when the pollutants are desorbed into the micellar phases (Cuypers et al., 2002). Because of their cold-water solubility, low critical micelle concentration (CMC) and relatively low microbial toxicity, nonionic surfactants have attracted particular interest in promoting desorption, microbial degradation, and uptake of pesticides from soils by plants (Gao et al. 2007; Wu et al., 2008; Harikumar et al., 2013). Humic substances are naturally occurring surfactants that have surfactant-like micelle microstructures that can increase the solubility of organic compounds and can potentially be used for enhancing the degradation of hydrophobic organic compounds (Holman et al., 2002). Also, cyclodextrins,

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(CDs) another type of solubility enhancing agent, have several characteristics that may allow them to be used for the remediation of pesticide-contaminated soils (Mohamed et al., 2008). Cyclodextrins are microbially produced cyclic carbohydrates that can form inclusion complexes with organic compounds in solution (He and Yalkowsky, 2004), increasing their water solubility. The torus α-1–4 linked glucose units have high aqueous solubility and contain a hydrophobic internal cavity, and are therefore available to form non-covalent host–guest inclusion complexes with a wide variety of organic contaminants of appropriate shape and size (Misiuk and Zalewska, 2009). Silicon (Si) is one of the most important elements for several plant species, and is particularly important for rice. The beneficial role of Si in enhancing plant resistance to various biotic (e.g. pest attack and pathogen infection) and a-biotic stresses (e.g. drought, salinity, metal ion toxicities, etc.) is particularly evident (Ma 2004; Liang et al., 2005). These beneficial effects of Si are attributed to both Si deposited in various tissues and soluble Si. High deposition of Si in tissue forms a physical barrier that enhances the strength and rigidity of the tissues (Ma and Yamaji, 2006). Si is deposited mainly in the cell lumen and the cell wall in the form of $SiO_2 \cdot nH_2O$ (Matichenkov et. al., 2000; Liang et al., 2005). Plants take up Si in the form of monosilicic acid, H_4SiO_4 (Ma and Takahashi, 2002). In the form of silicic acid, silicon is readily absorbed by plants in all soil types, and grown plants contain it as an appreciable, but a variable fraction of their dry matter (Epstein, 1994). There are numerous reports on Si suppressing plant diseases and pests (Cookson et al., 2007; Cai et al., 2008), in addition to improving plant nutrient uptake capability, thereby improving soil fertility (Schaller et al., 2012). To date, no reports have been published concerning the role of silicon dioxide (SiO_2) for enhancing the bioavailability and uptake of pesticides in contaminated soil Therefore, the present investigation is considered the first report for enhancing the bioavailability and phytoremediation of pesticides in contaminated soil by SiO_2. A larger number of inexpensive materials, including industrial and agricultural waste, have been used to remove different pesticides from aqueous solutions and soils for their safe disposal into the environment. These include rice bran and rice husk (Gupta et al., 2006; Akhtar et al., 2009). Rice bran has been shown to be particularly effective in the absorption of organic contaminants in soil due to its greater surface functional groups, *i.e.* amine, hydroxyl, carboxyl, and fiber carbonaceous (Adachi et al., 2001). It was proposed that the removal of contaminants such as organochlorine compounds, chemical mutagens, and carcinogens by rice bran was attributed to their uptake by intracellular particles called spherosomes (Sera et al., 2005). However, the microbial degradation and plant uptake of pesticides could be stimulated by the elemental nutrients in rice bran, thereby enhancing the biodegradation and bioavailability of pollutants in contaminated soil (Adachi et al., 2007). Therefore, assessing the removal of contaminants by rice bran amended soil is of importance. The objective of this study was to evaluate the capacity of *Plantago major* L. on the remediation of cyanophos-contaminated soil. The use of soluble silicon dioxide (SiO_2) and solubilization agents such as the surfactants, Tween 80, hydroxypropyl-β-cyclodextrin (HPβCD) and Liquid humic acid (HA) for enhancing the availability and uptake of cyanophos -contaminated soil by *P. Major* was evaluated. Additionally, the effect of adding rice bran to remove the pesticide cyanophos from the soil and uptake with plant was studied.

2. Materials and methods

2.1. Pesticide and plant materials

Cyanophos (Cyanox 50% EC) 0, 0-dimethyl 0-(4-cyanophenyl) phosphorothioate was obtained from the Central Agriculture Pesticide Laboratory, Agriculture Research Center, Dokki, Gaiza, Egypt.

Seedlings of the common broadleaf plantain (*Plantago major* L.) were used in phytoremediation experimental from meadow-land in Zagazig University, Zagazig, Sharkia Governorate, Egypt.

2.2. Experimental design

To evaluate the removal of cyanophos from the soil, nine treatments—each consisting of five replicates—were performed, as follows: (1) Cyanophos-contaminated autoclaved soil without plants. (2) T_1: Cyanophos-contaminated soil without plants. (3) T_2: Cyanophos-contaminated soil with *P. major* only. (4) T_3: Cyanophos-contaminated autoclaved soil with *P. major* only. (5)T_4: Cyanophos-contaminated soil with *P. major* and amended with soluble silicon dioxide (SiO_2), the so-called silica, at 750 mg/L for a total concentration of 187.5 mg kg. (6) T_5: Cyanophos-contaminated soil with *P. major* and amended with 2-hydroxypropyl-beta-cyclodextrin (HPβCD) at 1.0% (Chen et al., 2010). (7) T_6: Cyanophos-contaminated soil with *P. major* and amended with humic acid solution (HA) at 10 mg/L (humus WSG 90, Organist, Hungary), reportedly the critical micelle concentration of HA (Guetzloff and Rice, 1994). (8) T_7: Cyanophos-contaminated soil with plantain and amended with polyoxyethylene sorbitan monooleate (Tween 80) at 9.2 mg L, corresponding to 0.5 critical micelle concentration (CMC), where the CMC of Tween 80 was determined as 13–45 mg/L (Edwards et al. 1991; Mitton et al., 2012). (9) T_8: Cyanophos-contaminated soil with *P. major* and amended with rice bran at 1 g/ L.

In experiments (3)–(8), each pot contained one seedling of *P. major*. Each whole plant uptake experiment was performed in potted soil for 9 days. Air-dried sieved clay loam soil (organic matter, 1.79%, pH 7.8, electric conductivity 2.36 mS/m; Aboutwala, Minya al-Qamh, Sharqia, Egypt) was placed in plastic pots. The pots were filled with 500 g of air-dried soil. After planting, cyanophos dissolved in acetone was spiked into the 150 mL of distilled water used for irrigation to obtain original concentrations of 20 μg/g. Cyanophos concentration in irrigation water was added to the pots with caution from direct contact with the plant shoots. The treatment without cyanophos spiked into the soil acted as the control. After third and ninth day, exposed plants and the control were collected. Plant roots from the soil were rinsed in running tap water for two minutes and were blotted dry. The plants dissected into individual roots, shoots and then four grams of leaves and roots, in addition to twenty grams of soil were analyzed for the pesticide. All pots were watered with 50 ml tap water every four days with adding additional water when necessary.

2.3. Agents enhanced recovery of cyanophos

Laboratory studies were conducted to determine the adsorption equilibrium of cyanophos in soil in solutions of distilled water and the solubility enhancing agents, SiO_2, HPβCD, HA, Tw 80 and rice bran using a batch equilibrium technique. Batch equilibrium adsorption isotherms of cyanophos in soil in distilled water and aqueous solutions of SiO_2, HPβCD, HA, Tw 80, and rice bran at the same concentrations as above in Experimental design were evaluated with 40 μg/mL of cyanophos in 100 mL glass-stoppered conical flasks. The final volume in each flask was 20 mL by the addition of the requisite volumes of the cyanophos solution and distilled water or solutions of SiO_2, HPβCD, HA, Tw 80, and and rice bran. To these solutions, one gram of each soil was added, and the resulting suspensions were maintained at 25 °C for 21 h in an incubator following a period of shaking of 3 h. All experiments were conducted in duplicate. Preliminary studies showed that there was no measurable increase in the adsorption of cyanophos