

Remediation of heavy metals from soil using quartz sand functionalized with organic amino silanes

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The results of the research studies concerning the binding of heavy metals (HMs) by quartz sand functionalized with amino silanes have been described. The studies have been carried out on soils sampled from the areas affected by emissions from Copper Smelter and Refinery. The research aims to increase the food safety in the areas of industrial impact. The presence of polyamine chain in the hybrid materials obtained enables a binding of heavy metals (nickel, copper, cobalt). The best results are observed for the hybrid material having four amine groups (four coordination centers) per molecule. For this material the highest content after two extraction cycles (pH 7.0 and 5.0) is observed for copper (98.2%), but for other ions (nickel, cobalt) it is at least 85% of the initial amount of components available for plants.

Keywords: quartz sand, heavy metals, soil stabilization.

INTRODUCTION

Dynamic development of civilization and industry has brought about increasing pollution of the natural environment. The pollution of air, soil and water may lead to accumulation of harmful substances in living organisms including human. In this study the focus of our interest is the contamination of soil. In order to restore the ecological and economic utility of degraded environment land rehabilitation is applied according to the changed environmental conditions and local needs¹.

A removal of contaminants from soil can be carried out in two ways: *in situ* (by washing, aeration, bioremediation) or *ex situ* (by extraction, thermal purification, biodegradation, distilled or electrolytic purification, and many others)². For rehabilitation of soils contaminated by heavy metals, three main groups of methods have been proposed.

The first group is based on the formation of stable chelate complex or other coupling with heavy metals. In such a form the heavy metals are hardly available to plants. As the concentration of floated particles (colloid clay), organic matter and pH increases in soil, the toxic effects of heavy metals on plants and soil decrease because the metals undergo binding by buffer soil system and become inaccessible to plants³⁻⁵.

The major factor in determining the availability of heavy metals for plants is the sorption capacity of a given soil, which is determined by the quantity and quality of colloids forming the soil sorptive complex. The humus content in soil is particularly controlled in agricultural areas contaminated with heavy metals, as humus is able to cause regresses of metals strong enough to prevent the negative effects of soil contamination. Previous research studies⁶ have confirmed that the organic matter of soil is able to bind heavy metals in the presence of plant material in soil. Therefore, the metal content in further elements of trophic chain is much lower⁷⁻⁹. The other complete source of organic matter in soils could be brown coal and organic-mineral fertilizers from brown coal^{10, 11}.

The second group of rehabilitation methods includes techniques that partially remove heavy metals (biologically, chemically, electrochemically). However, excluding biological methods, the others are very expensive and do not guarantee total purification, i.e. they do not restore the original chemical composition of soils from before the pollution. Additionally, chemical and electrochemical techniques of purification lead to degradation of biological activity of soils⁴.

The elimination and isolation of heavy metals is in general difficult. Phytoremediation^{12, 13} is an inexpensive, “green” treatment, employing three purification methods: phytoextraction^{4, 5} (plants remove heavy metals from soils and transport them up into above-ground elements); rhizofiltration^{14, 15} (absorption, concentration and precipitation of heavy metals by cultivated plant roots); phytostabilization^{15, 16} (long-term containment and stabilization of heavy metals in soils). The method of phytoextraction is based on the use of plants from the group of hyperaccumulators^{17, 18}, having small biomass, and some species of trees and shrubs collecting large amounts of metals from soil. Phytoextraction efficiency can be increased by the induced hyperaccumulation process. The heavy metals are released by soil acidification or an addition of chelate complexing agents (EDTA, DTPA, citric acid, tartaric acid, aminoacids)¹⁸⁻²⁰. Induced hyperaccumulation raises many concerns. There is a danger of washing out of activated forms of metals into groundwater and their interaction with flora and fauna of the soil²¹.

Heavy metals can be also removed by natural or synthetic adsorbents (e.g. bentonite, zeolite) placed in the topsoil²¹⁻²⁴. Another method of land rehabilitation is removal of topsoil and its mixing with pure soil. However, it is also a very expensive technique and useful only for point pollution²⁰⁻²⁴. The last group of soil rehabilitation methods is based on the change of land use by planting shrubs and trees.

All soils strongly polluted with heavy metals should be excluded from agricultural production. Only economic plants should be cultivated on polluted soil (e.g. flax, hemp, purple willow, energetic willow, miscanthus, potatoes for processing alcohol and rape)²¹⁻²⁴.

Previously, we have studied the complexing ability of the magnetic²⁵ and non-magnetic²⁶ inorganic surfaces modified with amine-silanes and with other organic compounds²⁷. The systems studied were able to extract heavy metals from water solutions. This paper describes the results of soil rehabilitation by quartz sand functionalized with silanes having polyamine substituents that are capable of binding of metal ions and form complexes of high stability constants.

EXPERIMENTAL

Quartz sand was functionalized with five amine-silanes (Fig. 1), containing different number of ethylene amine units (0–4).

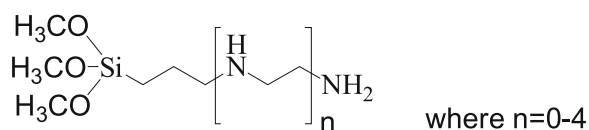


Figure 1. Schematic representation of amine-silanes 1-5 applied for functionalization of quartz sand

Silanes 1–3 ([3-Aminopropyl] trimethoxysilane; [3-(2-Aminoethylamino)propyl] trimethoxysilane and 3-[2-(2-Aminoethylamino)ethylamino]propyl trimethoxysilane respectively) were commercial products of Aldrich. Silanes 4-5 ([1,4,7,10-tetraazatridecane] trimethoxysilane and [1,4,7,10,13-pentaazahexadecane] trimethoxysilane respectively) were substitution products obtained by a reaction of amines (Triethylenetetramine or Tetraethylenepentamine respectively; Aldrich) with (3-Chloropropyl) trimethoxysilane (Aldrich) under standard reaction conditions (heating of substrates under reflux condenser; separation of polyamine hydrochloride; distillation of reaction product).

A procedure of quartz sand functionalization

Quartz sand (Aldrich) with granulation 0.1–0.3 mm was acidified (5 mol dm⁻³ hydrochloric acid water solution), washed and dried. Then it was functionalized with amino-silanes upon mixing process in alcoholic solution (ethanol; POCH), using 0.1 mol of silane per 1 kg of quartz sand. After solvent evaporation the hybrid material was obtained.

The hybrid materials obtained (1–5) were capable of binding 15 mg of metal ions per 1g of the material (based on titration with EDTA).

The IR spectra of the hybrid materials were recorded on IFS 66 v/s FT-IR spectrophotometer from Bruker, equipped with a MCT detector (128 scans, resolution 2 cm⁻¹).

A procedure of metal extraction from soil samples

A portion of 25 g of soil sample was mixed with 1 g of the hybrid material. Then redistilled water (2.5 m³) was added and left for 4 days, during which the sample was stirred every day and the soil moisture was kept constant. After that time the soil sample was twice extracted with 10 mL of CH₃COONH₄ (1 mol dm⁻³) in room temperature (20°C) for pH 7.0 and metal content in soil was measured. Metal content was tested again after double extraction with 10 mL of CH₃COONa (1 mol dm⁻³) and soil acidification (CH₃COOH) to pH

5.0. Metal concentration in soil samples was determined using X-ray fluorescence (XRF) spectrometer (MiniPal) from Philips calibrated for quantitative analysis based on soil reference materials (LGC standards).

RESULTS AND DISCUSSION

The generalized formula of functionalized quartz sand with amino-silanes 1–5, the hybrid material, is presented in Figure 2, where n = 0–4 and concentration of silanes is 0.1 mol of silanes per 1 kg of quartz sand.

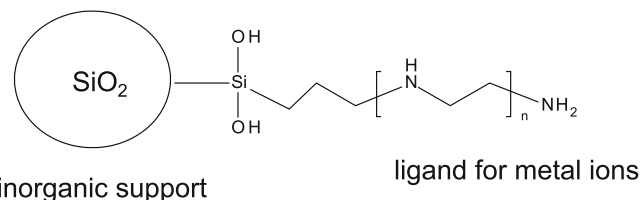


Figure 2. Schematic representation of the sorbents studied

The hybrid material is composed of two elements, i.e. inorganic core, whose surface was functionalized using silanization procedure with organic part capable of forming stable complexes with metal ions.

The formation of organic layer on quartz sand was confirmed by infrared spectroscopy. The hybrid materials studied gave similar spectra differing only in the signal intensity. Figure 3 shows exemplary spectrum of hybrid material 1. A band appearing at 2930 cm⁻¹ was assigned to the stretching vibrations of alkyl groups. The broad band between 3400 to 3200 cm⁻¹ was assigned to the O-H stretching frequencies of the surface silanol groups and adsorbed water. Therefore a typical N-H stretching band in the range 3400 to 3500 cm⁻¹ was difficult to identify. The other signals observed were characteristic for the inorganic support.

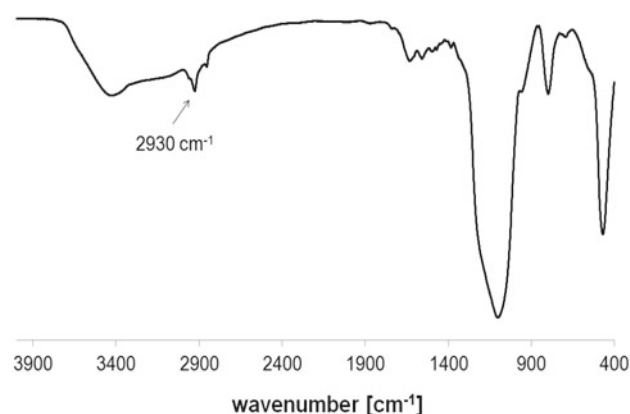


Figure 3. FTIR spectrum of hybrid material 1

In the area of industrial impact of extractive industry and metallurgy the soil is characterized by higher content of metals when compared to other regions. In Poland the concentration of copper, lead, zinc, nickel, cobalt and cadmium in soil, is monitored in the area of copper smelter impact. Total content of metals in soils sampled from the areas affected by emissions from the Głogów Copper Smelter and Refinery was 382 mg/kg, including 242 mg Cu/kg, 96 mg Pb/kg, 34 mg Zn/kg, while the contents of the other elements were much lower (below

10 mg/kg)^{28, 29}. Heavy metal content in individual fractions of soil depends on the content of clayey fraction, while the affinity of different metals to soil components is related to their affinity to individual soil components, i.e. humic acids, hydrated iron oxides, kaolinite, illite or montmorillonite. Sequential analysis of soil samples collected from the areas affected by emissions from copper smelter was carried out according to the Tessier method³⁰ (Table 1) and the results demonstrated that the content of each impurity was different in individual soil fractions. The highest content of heavy metals was found in fractions (F₁-F₄), in which metal assimilation by plants is the highest, while in fraction F₅ that is unavailable for plants, the metal concentration was 20% of that in fractions F₁-F₄. The content of heavy metals in fraction F₁, which is characterized by the easiest capability of metal exchange in soil and assimilation of heavy metals by plants, determines the applicability of the soils for food production. If the concentration of heavy metals in this fraction is high, the land can be only used for industrial crops.

Earlier studies on the application of different silane derivatives in the form of solutions doped to soil, demonstrated that N¹- (3-Trimethoxysilylpropyl) diethylenetriamine had the strongest capability of permanent binding of heavy metals, in comparison with that of (3-Aminopropyl) trimethoxysilane and [3-(2-Aminoethylamino) propyl] trimethoxysilane²⁹. The application of silane solutions spraying for permanent binding of metals in soil is one of two methods feasible for recultivation of agricultural areas. The other method described in this paper, consists in an addition of hybrid material, i.e. quartz sand functionalized with silanes – products of earlier industrial (laboratory) synthesis, to polluted soil.

The soil samples used in the research studies contained 95.9 ppm of copper; 67.8 ppm of cobalt and 54.4 ppm

of nickel. Each sample was extracted with 1M solution of CH₃COONH₄ (pH 7.0). Then it was doubly extracted with 1M solution of CH₃COONa, acidified with CH₃COOH to pH 5.0. The metal content after extractions was determined for pH 7.0 and 5.0. The results represent the average of several repeated series of experiments and they are collected in Table 2.

The results obtained show that addition of hybrid materials 1–5 can significantly influence the metal content in soil after extraction. The properties of the materials discussed are strongly dependent on the organic fragment that is responsible for complexing of metal ions. After first extraction cycle (pH 7.0), the content of heavy metals in comparison with the initial amount of exchangeable components and elements available for plants, ranged from 23% (hybrid material 1) to 1.8% (hybrid material 4) for copper; 28.8% (hybrid material 1) to 10.8% (hybrid material 4) for cobalt; 19.4% (hybrid material 1) to 7.4% (hybrid material 4) for nickel. The effectiveness of metal ion binding by hybrid material 5 was lower (a few percent) than for hybrid material 4.

Similar results were obtained after extracting soil samples with a solution of pH 5.0. After the second cycle of this extraction the content of heavy metals in comparison with the initial amount of exchangeable components and elements available for plants, ranged from 48% (hybrid material 1) to 5% (hybrid material 4) for copper; 62.5% (hybrid material 1) to 14.6% (hybrid material 4) for cobalt; 55.1% (hybrid material 1) to 10.7% (hybrid material 4) for nickel. Again the effectiveness of metal ion binding by hybrid material 5 was lower (a few percent) than for hybrid material 4.

The results of our research studies show that quartz sand functionalized with silane 4 demonstrates the best effectiveness towards binding of copper, cobalt and nickel ions. Four amine groups per a molecule and thereby

Table 1. Extraction conditions of different forms of heavy metals in soil

Fraction	Form of metal	Extraction conditions
F ₁	exchangeable metals	10 cm ³ 1M CH ₃ COONH ₄ (pH 7.0), shaking time 1h, temp. 20°C
F ₂	metals associated with carbonates	20 cm ³ 1M CH ₃ COONa acidified with CH ₃ COOH to pH 5.0, shaking time 5 h, temp. 20°C
F ₃	metals associated with hydrated oxides of iron (Fe) and manganese (Mn)	20 cm ³ 0.04M NH ₂ OH·HCl soluble in 25% CH ₃ COOH, shaking time 5 h, temp. 95°C
F ₄	metals associated with organic matter	5 cm ³ 0.02 M HNO ₃ + 5 cm ³ 30% H ₂ O ₂ (pH 2.0), shaking time 2 h, temp. 85°C 5 cm ³ 30% H ₂ O ₂ (pH 2.0), shaking time 3 h, temp. 85°C 10 cm ³ 3.2 M CH ₃ COONH ₄ in 20% HNO ₃ , shaking time 0.5 h, temp. 20°C
F ₅	metals associated with aluminosilicates	3 cm ³ 10 M HNO ₃ + 3 x 2 cm ³ H ₂ O ₂ , shaking time 1 h + 10 cm ³ H ₂ O, shaking time 0.5 h, boiling temp.

Table 2. The metal content [ppm] in soil after an addition of hybrid materials 1–5 (25 g of soil per 1g of hybrid material)

Hybrid materials	1			2			3			4			5		
	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni	Cu	Co	Ni
Initial metal content in soil	95.9 +/- 0.1	67.8 +/- 0.1	54.4 +/- 0.1	95.9 +/- 0.1	67.8 +/- 0.1	54.4 +/- 0.1	95.9 +/- 0.1	67.8 +/- 0.1	54.4 +/- 0.1	95.9 +/- 0.1	67.8 +/- 0.1	54.4 +/- 0.1	95.9 +/- 0.1	67.8 +/- 0.1	54.4 +/- 0.1
Metal content in soil after extraction pH = 7.0	73.8 +/- 0.1	48.3 +/- 0.1	44.4 +/- 0.1	80.6 +/- 0.1	47.0 +/- 0.1	48.2 +/- 0.1	85.0 +/- 0.1	58.8 +/- 0.1	46.4 +/- 0.1	94.2 +/- 0.1	60.5 +/- 0.1	50.4 +/- 0.1	90.7 +/- 0.1	57.8 +/- 0.1	38.0 +/- 0.1
%(ww.)*	77.0	71.2	81.6	84.0	69.3	88.6	88.6	86.7	85.3	98.2	89.2	92.6	94.6	85.2	69.9
Metal content in soil after extraction pH = 5.0	49.9 +/- 0.1	32.2 +/- 0.1	24.4 +/- 0.1	55.3 +/- 0.1	37.4 +/- 0.1	24.7 +/- 0.1	61.2 +/- 0.1	47.9 +/- 0.1	38.9 +/- 0.1	91.1 +/- 0.1	57.9 +/- 0.1	48.6 +/- 0.1	85.7 +/- 0.1	50.8 +/- 0.1	32.8 +/- 0.1
%(ww.)*	52.0	47.5	44.9	57.7	55.2	45.4	63.8	70.6	71.5	95.0	85.4	89.3	89.4	74.9	60.3

* mass percentage metal content relative to its initial amount

four coordination centers are optimal for formation of stable complexes with metal ions. Introduction of another coordination centre in a polyamine chain (hybrid material 5) does not increase the effectiveness of ion binding in soil.

Heavy metals are kept in soil through exchangeable chemical, physical and biological sorption. Addition of quartz sand functionalized with amine-silanes increases chemical sorption of heavy metals and reduces the mobility of these metals in environmental conditions as a consequence of complex formation.

Currently applied technique of soil stabilization of HMs by changing of pH does not guarantee their permanent blocking in a sorptive complex. The method described in this paper enables doping functionalized quartz sand to soil in a completely controlled way in terms of quantity and safety. The hybrid material has analogous structure to forms available in soil, thus it does not influence soil quality to a significant degree. The most effective material described in this paper was hybrid material 4, which demonstrated excellent properties of binding of copper, cobalt and nickel in soil, making these metals much less available to cultivated plants.

CONCLUSIONS

The inorganic-organic materials, quartz sand and amine-silanes was obtained as a potential hybrid materials stabilizing heavy metals in soil. The presence of a polyamine chain enables binding of heavy metals (nickel, copper, cobalt) and the best results are observed for the hybrid material having four amine groups (four coordination centers) per molecule.

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