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Polymeric forms of Al_{13} and silicon compounds as unconventional binding agents for some toxic metals in soils

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Abstract. Own studies and literature data allowed for the evaluation of sorbents in view of the general verification criteria, which are necessary for any sorbent to be applied with no harm to the environment. Polymeric forms of Al_{13} and Si compounds are examples of mineral sorbents that influence metals' toxicity in the environment.

Key-words: polymeric forms of Al_{13} , Si compounds, metals binding

1. Introduction

Gentle techniques for the remediation of toxic metal-contaminated soils aim at using immobilizing agents that influence soil fertility with no damage on its structure (Badora et al. 1998; Badora 1999, 2002a,b). The basic criteria of an immobilizing agent are based on (i) the lack of toxicity towards living organisms, (ii) no change of binding agents or the soil fertility, and (iii) the features of the immobilizing toxic elements.

Polymeric forms of Al_{13} and Si compounds are examples of mineral sorbents, whose influence on heavy metals' toxicity within the natural environment has been recognized in part (Ludwig 1990; Furrer 1993; Lothenbach et al. 1997; Lothenbach et al. 1998; Badora 2001a). Own studies (Badora et al. 1998; Badora 1998a,b,c, 1999, 2001a,b, 2002a,b; Badora, Grenda 2000, 2002; Badora 2010, 2011) and literature data allowed for analyzing

the above sorbents in view of the general verification criteria, which is necessary for the sorbents to be applied with no harm to the environment.

Under some circumstances, Si compounds can control the content of toxic ions within soil solution through neutralizing the negative effects of Al and Mn for plants (Corrales et al. 1997; Marschner 1998; Exley 1998; Hodson, Sangster 1999; Badora, Grenda 2000, 2002; Heal 2001; Iwasaki et al. 2002; Kitao et al. 2002; Badora 2003).

The current paper deals with the evaluation of Al, Mn, and selected heavy metals' detoxication mechanisms by polymeric forms of Al_{13} and Si compounds based on literature references and own studies.

2. Chemistry of unconventional binding agents

2.1. Polymeric forms of Al_{13}

Due to its characteristic structure, Al_{13} generates exchange sites in a form of hydroxyl moieties, resulting from the deprotonation process of water (Furrer 1993). They are efficient sites for heavy metals' binding comparable to those of specific sorption proceeding under appropriate conditions on some one-and-a-half oxides (Furrer 1993; Badora 1999). According to Furrer (1993), complexing heavy metals by poly-nucleus Al forms is an inseparable link associated with Al geochemistry. Under the circumstances of long-term processes related to the complexation of heavy metals by Al_{13} , they can be permanently trapped in the lattice of aluminosilicates and Al hydroxides.

According to Bertsch (1987), the process of poly-nucleus specimens' formation, including the most cited tridecamer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, depends on three factors:

- the Al concentration in a soil solution
- the OH^- to Al ions ratio (n_0)
- the neutralization rate

The author claims that the monomeric Al form, i.e. $Al(OH)_4^-$, is the precursor of Al_{13} production.

The toxicity of the polymer under water culture condition arouses much controversy. Some authors have applied tests for verifying Al_{13} toxicity fitting the relative root indicator (RRI) for wheat growth depending on the alkalinity coefficient n_0 (Parker et al. 1988). Using the example of RRI dependence on the alkalinity coefficient (n_0), the authors underlined that at $n_0 = 2.2$, i.e. the value at which the formation of tridecamer was the most efficient, the relative root growth reached its minimum level, which clearly provides the toxicity of this Al form. Similar conclusions were drawn by Parker and Pedler (1998) from tests with maize. Other authors (Wallace 1992; Wagatsuma et al. 2001) reported the toxic influence of polymeric Al forms on oat tolerant towards mono-nucleus forms. The opposite opinion was presented by Badora (1999), who did not observe any Al_{13} toxicity of $0.10 \text{ mmol} \cdot \text{dm}^{-3}$ concentration in hydroponic tests with pea.

Among the many publications on Al_{13} , only Hunter and Ross (1991) found the presence of polymer in the soil solution. They used the Nuclear Magnetic Resonance technique (^{27}Al -NMR) to determine this Al form in their study; however, their results were impaired due to the high content of organic carbon exceeding $800 \text{ g} \cdot \text{kg}^{-1}$ soil, which could bias the measurements (Taniguchi et al. 1999).

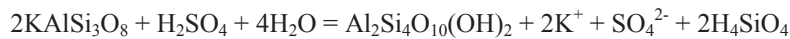
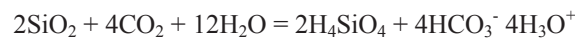
Saigusa and Matsumoto (1995) reported that Al_{13} may be present in the soil solution, although it is strongly absorbed by montmorillonite. Taniguchi et al. (1999) also proved that the probability of forming such complex structures as tridecamer in soil solutions is very low. The factor that determines the polymer formation is the Si:Al ratio. The same authors claimed that the critical value of this ratio is 0.24, under which there are no thermodynamic grounds for tridecamer formation. According to these scientists, the majority of worldwide soils showed the mentioned ratio from 1 to over 1,000.

Toma et al. (1999) discovered conditions corresponding in theory to polymer formation. In order to decrease the acidity during the application of gypsum on andosols, the process was expressed by the authors as self-liming effect. The emergence of Al_{13} forms was expected after partial neutralization of the soil solution; however, any Al_{13} forms present in the soil solution were found after applying the ^{27}Al -NMR technique.

Other researchers (Furrer 1993; Lothenbach et al. 1997; Badora et al. 1998) underlined that such environmental conditions as the ionic strength (I) and acidity (pH) of a solution are important during the Al_{13} formation. According to Parker et al. (1988), tridecamer is formed in water solutions of pH = 5.2 and $n_0 = 2.0$, while Bertsch (1987) reported the formation of that Al form at $n_0 = 2.5$, and Lothenbach et al. (1997) at pH = 5.4 – 6.0 and $n_0 < 2.9$. However, all these authors univocally found that amorphous $\text{Al}(\text{OH})_3$ was formed above the quoted pH values. The process takes place as a result of further Al_{13} deprotonation (Furrer 1993). The durability of Al_{13}^{7+} structure under conditions of water cultures is high, due to a lack of proton access to the tetrahedron nucleus of AlO_4 surrounded by 12 octahedron units (Parker et al. 1988; Lothenbach et al. 1997). Such structure is practically durable for 6 months due to the properties described above (Lothenbach et al. 1997).

2.2. Silicon compounds

Si is the second most commonly spread element within the earth's crust. The mobile form of Si in the soil solution consists of orthosilicic acid $(\text{H}_4\text{SiO}_4)^2$. Its mobility depends on the acidity as well as the one-and-a-half oxides content. Orthosilicic acid is formed as a product of the chemical erosion of primary minerals, mainly quartz and orthoclase (Exley 1998; Marschner 1998).



In general, the higher both the one-and-a-half oxides content and the pH, the lower the mobility of orthosilicic acid. Under conditions of elevated pH, condensation and polymerization product occurs in the form of amorphous silica (Exley 1998).



Si is taken up by plants in extremely readily forms as SiO_4^{4-} (Wallace 1992). Its content in plant's dry matter is comparable to that of macronutrients (Rafi, Epstein 1999). According to Marschner (1998), Si is considered as an element that has a positive effect on plant's growth (beneficial element), because it meets the following criteria:

- stimulates plant growth
- is essential for some plant groups

Referring to the Si uptake, plants can be divided into three groups:

- those taking up large amounts of Si, $100 - 150 \text{ g} \cdot \text{kg}^{-1}$ of above ground parts dry matter, e.g. rice
- those containing $10 - 30 \text{ g} \cdot \text{kg}^{-1}$ in dry matter of above ground parts, e.g. sugar cane and most cereals
- those containing below $5 \text{ g} \cdot \text{kg}^{-1}$ of Si in dry matter of above ground parts, namely papilionaceous plant species

Some authors (Exley 1998; Marschner 1998; Perry, Keeling-Tucker 2000) underlined a positive influence of Si on plants' metabolism, particularly in the case of silicophilous plants (with enhanced needs for Si compounds).

The positive effects of Si can be listed as follows:

- endoderm silification (forming a thin Si coating that prevents pathogen and parasite penetration through the roots)
- building a thin coating on the leaf epidermis, protecting against pathogen invasion
- inducing microelements' uptake (Zn, Mn) under conditions of excessive phosphate levels in the environment
- participating in lignin's synthesis
- controlling the rigidity and elasticity of cell walls
- controlling the rigidity of the leaf blade by eliminating the negative influence of nitrogen over-fertilization
- improving the photosynthesis rate by controlling leaf blade exposure (leaf blade hardening) to solar radiation
- increasing chlorophyll content
- lowering the requirements for water (more economic water balance and lower transpiration coefficient)

Si's influence on plants' metabolism plays quite an important role in detoxicating the excessive quantities of Al, Mn, Fe (Baylis et al. 1994; Marschner 1998; Iwasaki et al. 2002) and heavy metals (Chen et al. 2000; Badora 2001a,b; Badora, Grenda 2002).

3. Metals *versus* unconventional binding agents

3.1. Polymeric forms of Al_{13} and heavy metals' toxicity

Some authors (Furrer 1993; Lothenbach et al. 1997; Badora et al. 1998) reported higher efficiency of Zn, Ni, and Cd binding by Al_{13} , while the tridecamer was less effective towards Cu and Pb. When $\text{Ba}(\text{ClO}_4)_2$ was added in excess to evaluate the durability of the achieved bindings, Cd appeared to be re-mobilized to a considerable degree. Lothenbach et al. (1997) found that the bonds between Al_{13} , as well as the Zn and Ni ions were of a strong coordinate character. In a study performed by Badora et al. (1998), similar results were

obtained upon soil material contaminated with Zn and Cd in the presence of various Al_{13} quantities. The authors univocally concluded that the Al_{13} agent was characterized by better binding efficiency towards Zn, as compared to Cd.

Study by Ludwig (1990) outlined a prominent increase of copper adsorption on Al_{13} at pH 5.5, while up to 95% of the total copper was adsorbed at pH 6.2. According to Lothenbach et al. (1997), the issue of metals' complexation by Al_{13} under conditions of appropriate pH should be associated with the metals' properties (their ability to hydrolysis) and the features of Al_{13} itself, related mainly to its deprotonation. The authors discovered a close dependence between the hydrolysis constant for the tested metals (Cu, Pb, Ni, Cd, and Zn) and the pH_{50} indicator (which informs that 50% of the total metal quantity introduced into a solution was adsorbed at a given pH). Lothenbach et al. (1997) stated that the most optimum pH value, at which Al_{13} manifested its best efficiency in Cu, Ni, Zn, Pb, Cd adsorption, was 6.0 – 7.5.

Badora et al. (1998) reported clear Zn re-mobilization above $0.4 \text{ mmol Al}_{13} \cdot \text{kg}^{-1}$. The Al_{13} rates higher than $0.4 \text{ mmol Al}_{13} \cdot \text{kg}^{-1}$ soil were tested by the authors but did not show any immobilization effect, rather they initiated metals' mobilization. The most efficient Zn ions immobilization was reached when the metal/ Al_{13} ratio amounted to 1:1, within the pH range 6.0 – 6.5. The authors elucidated the effect of Zn immobilization at higher Al_{13} levels by the fact that the excess of Al_{13} probably competed with the Zn ions for active centers on the organic substance surface. The formation of Zn complexes with low-molecular organic acids could occur as well.

The process of heavy metals' complexing by Al_{13} , as well as the influences of other components is difficult. A prominent interferential effect of organic substance on Zn and Cd binding by the presence of tridecamer Al_{13} was found (Badora et al. 1998; Lothenbach et al. 1998). Furthermore, the binding efficiency even arose after the destruction of organic matter with H_2O_2 . On the other hand, other reports (Badora 1998a,b, 2002a,b) revealed that the addition of organic substance in the form of citric and humic acids had no significant effects on Cd and Zn immobilization by Al_{13} , during experiments carried out under hydroponic conditions.

3.2. Silicon compounds versus aluminum and manganese toxicity

The formation of aluminosilicate complexes was discovered in water solutions. The complexes were assumed to be precursors of protoimmogolites and alophanes (Hodson, Sangster 1999). Their formation was considered as evolutionary mechanisms for prevention against excessive amounts of toxic Al forms (Perry, Keeling-Tucker 2000).

Exley (1998) stated that the formation of Al forms depends on the Si:Al ratio and pH of the soil solution. At pH 4.0 and at the concentrations of $50 \mu\text{mol Al} \cdot \text{dm}^{-3}$ and $1000 \mu\text{mol Si} \cdot \text{dm}^{-3}$, no aluminosilicate complexes were observed. Meanwhile, these complexes were prominently formed at pH 5.5 and concentrations of $1000 \mu\text{mol Al} \cdot \text{dm}^{-3}$ and $\mu\text{mol Si} \cdot \text{dm}^{-3}$ (Perry, Keeling-Tucker 2000). Exley (1998) divided the aluminosilicate forms into two groups depending on the pH value: below pH 4.0, he reported the presence of soluble and stable forms (soluble-HAS); while above pH 4.0, he distinguished the insoluble and stable forms (insoluble-HAS).

The mechanisms elucidating the lower toxicity of Al compounds in the presence of Si are contradictory. Some studies claim that the detoxication mechanism occurs in the soil solution (Baylis et al. 1994; Badora 2002a,b), while others assume that it occurs within the plant (Cocer et al. 1998; Hodson, Sangster 1999).

Probably, the mechanism of Al detoxication by Si compounds in the soil solution consists of hydroxyaluminosilicate species. These complexes become hardly mobile (Baylis et al. 1994). Badora (2001b, 2002a,b) also reported that in hydroponic the decrease of soluble Al forms occurred after adding meta-silicates.

The mechanisms of Al detoxication by Si compounds in the plant are given as follows:

- forming mobile Al – Si complexes in apoplast in a form of HAS or aluminosilicates that do not penetrate maize and wheat symplast (Corrales et al. 1997; Cocer et al. 1998; Hodson, Sangster 1999)
- forming Al-Si deposits in epidermis and mesophyll of coniferous leaves
- forming Al-Si complexes in the vacuoles of maize root cells (Hodson, Sangster 1999)
- enhancing the retention abilities of cell walls (Iwasaki et al. 2002)
- controlling the anion–cation balance within the plant (Wallace 1992)
- reducing the toxicity in an indirect way: during Si ions uptake, the OH-ions are equivalently released into the soil environment, and the consequence is the precipitation of Al hydroxides (Wallace 1992).

The mechanism for lowering manganese toxicity occurs mostly within the plant (Marschner 1998; Iwasaki et al. 2002). According to Marschner (1998), the most characteristic symptom of Mn toxicity – brown spots on the leaf blade surface – is inhibited as a result of the uniform distribution of Mn compounds in the presence of Si compounds. It should be emphasized that the polyphenols responsible for the brown color of spots produced are not oxidized due to the detoxication action of Si compounds. Iwasaki et al. (2002) reported that the mechanism of preventing brown spot formation on the leaf blade surface by Si compounds is indirect. Iwasaki et al. (2002) also underlined the enhancement in the binding properties of cell walls in the presence of Si compounds. The quantities of manganese extracted from cell walls by using DTPA were higher in plant samples with Si, compared to those with no Si added (Iwasaki et al. 2002).

3.3. Silicon compounds versus heavy metals' toxicity

Some concern was devoted to the issue of lowering the heavy metals' toxicity in the presence of Si compounds. McBride (1994) and McBride et al. (2000) reported that the evaluation of a direct influence of silicates on decreasing the mobility of heavy metals is difficult. Therefore, the effect of the lower solubility of heavy metals may not be a direct cause of the Si compounds' influence. Badora (2002a,b) obtained similar results when observing the increase of pH value after applying the silicates in order to immobilize Zn and Cd ions. Perry and Keeling-Tucker (2000) speculated that the bond between bivalent metals and Si compounds may be formed through a single SiOH group of polymeric Si form, while direct binding between orthosilicic acid and Ca^{2+} ion is impossible within the pH range usually found in biological systems. The mechanism of reducing the metal ions' mobility in the soil solution by polymeric Si forms may also occurs on a basis of co-precipitation (Perry, Keeling-Tucker 2000). A significant influence of Si compounds on

decreasing the solubility of Cd ions and their uptake by rice and Chinese cabbage was confirmed by Chen et al. (2000). These authors applied multiple regression analysis to verify the dependence, in which Cd concentration in dry matter of the above-ground parts of the plants was the dependent variable, while the active forms of Si in the soil solution, the pH value, and the interaction of both parameters were the independent variables. High determination coefficients confirmed a close interdependence between the active Si form and pH versus the Cd content in the dry matter of the test plants:

$$Y_1 = 18.54 - 6.352 (\text{Si}) - 2.1531 (\text{pH}) + 0.812 (\text{Si} \times \text{pH}); R^2 = 0.630, (P < 0.001)$$

$$Y_2 = 950 - 257.6 (\text{Si}) - 127.1 (\text{pH}) + 35.53 (\text{Si} \times \text{pH}); R^2 = 0.960, (P < 0.001)$$

where:

Y_1 – Cd content ($\text{mg} \cdot \text{kg}^{-1}$ DM) in the above-ground parts of rice

Y_2 – Cd content ($\text{mg} \cdot \text{kg}^{-1}$ DM) in the above-ground parts of Chinese cabbage

Si – content of active Si form in the soil solution ($\text{mg SiO}_2 \cdot \text{kg}^{-1}$ soil)

4. Conclusions

The binding mechanisms of Al_{13} forms and Si compounds applied for heavy metals and Al toxicity are complex and nonuniform, and therefore require further investigation. The analysis of the structure and chemistry of the tested binding agents indicates their selective affinity to various toxic metals. The sorbent dose and environmental conditions such as the pH, sorption capacity of the soil, presence of organic substance, and the synergistic and antagonistic processes affected the mobilization and immobilization of toxic metals.

Heavy metals and Al mobility is associated with the risk of their intensified uptake and incorporation into the food chain. Therefore, searching for new detoxication methods, including attempting to apply different unconventional sorbents, is an important issue.

Polynuclear Al, Al_{13} , is an agent that can be used in fewer circumstances and leads to higher investigation costs. However, the mechanism of its pathways in soil is very important, because it helps to improve understanding of the processes of toxic metals' mobilization and translocation in the soil. A prominent interferential effect of organic substances on Zn and Cd binding by the tridecamer Al_{13} was found. On the other hand, the addition of organic substances in the form of citric and humic acids had no significant effects on Cd and Zn immobilization by Al_{13} during experiments carried out under hydroponics.

Si is counted towards elements that positively affect the plant's growth (beneficial element), because it meets the following conditions: stimulates the plant's growth, and is essential for some plants. Besides the positive mechanisms of Si on plant's metabolism, it also plays a very important role in detoxicating excessive amounts of Al, Mn, or heavy metals.

Mechanisms elucidating the lower toxicity of Al compounds in the presence of Si are contradictory. One group of scientists claims that the detoxication mechanism takes place in the soil solution, while other authors assume that all detoxication mechanisms occur within the plant. The mechanism for lowering Mn toxicity occurs mostly within the plant.

The evaluation of the direct influence of silicates on the decreased mobility of heavy metals is difficult. Therefore, the effect of the lower solubility of heavy metals may not be a direct cause of the Si compounds.

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