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Studies on platinum (IV) ions sorption in loess and loamy soils

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Abstract. The aim of the experiment was to study the sorption of platinum ions in loess and loamy soils in the presence of Pb(II) and Cd(II) ions, in relation to temperature, incubation time and concentration of added Pt(IV) ions. Soil samples were treated with solutions of platinum ions in the form of $PtCl_4$ containing 20, 40, and 200 mg Pt(IV) dm^{-3} and with 100 mg Pb(II) dm^{-3} as $Pb(NO_3)_2$ and 50 mg Cd(II) dm^{-3} as $CdCl_2$, and incubated at two temperature levels: 5 and 20°C over periods of 1, 2, 3, 4, 5, and 6 months. The Pt(IV) ions content was determined in the filtrates by means of the voltamperometric method, with additional concentration. On the basis of the obtained results, it was found that the sorption of platinum (IV) ions in soils depends on all the factors used in the experiment.

Keywords: platinum ions, sorption, loess soil, loamy soil

INTRODUCTION

At present, all irregularities and disturbance of general equilibrium in the biosphere result from anthropogenic activity (Woźniak, 2000). Motor traffic is one of the reasons responsible for the situation. Excessive amounts of heavy metals accumulated in plants and soils are the most dangerous effect of motor transport affecting the adjoining agricultural areas. So far lead, whose excess in air, soil and plants is responsible for chronic diseases in people and animals, has been considered to be the most harmful (Curzyło, 1995; Helmers *et al*., 1995).

The concentrations of conventional heavy metals like lead in urban ecosystems have ceased growing since the peak in the 60's and 70's of the 20th century. This is most of all the result of automobile exhaust purification by catalytic converters, which requires the use of unleaded fuel. At the same time there has been observed an increase in the emission of platinum group metals (Sures *et al*., 2002) used as active elements reducing the emission of hydrocarbons, carbon oxide and nitrogen oxides. Constantly increasing platinum concentration in the street dust and in soils close to frequented roads is still being observed (Heinrich *et al*., 1996; Helmers and Kummerer, 1999; Zereini *et al*., 1997). According to Schäfer and Puchelt (1998), the platinum content in the soil layer of 0-2 cm in areas adjacent to the traffic lane is from 30 to several hundred $\mu g\ kg^{-1}$. Decrease in platinum group metals concentrations with the distance from road is similar to that of other elements originating from the car emission (Pb, Zn, Cu). In the distance about 20 m they are slightly larger than those of the geochemical background (Schäfer *et al*., 1996).

Platinum is believed to be emitted in metallic form, with a small amount of soluble fraction (from 1% by Artelt *et al*., (1999) to 10% by Moldovan *et al*., (2002)). Therefore, most of the emitted platinum is not directly accessible to living organisms. The presence of Pt in grass (Helmers and Mergel, 1997; Helmers *et al*., 1998) and vineyards (Alt *et al*., 1997) situated close to the roads indicates that the emitted platinum is transformed into bioavailable forms. This transformation can take place in the air, on the road surface area, or in the soil where Pt is deposited (Lusting, 1997).

The aim of the experiment was to study the sorption of platinum ions in two soils, with relation to temperature, incubation time, concentration of added Pt(IV) ions, and in the presence of Pb(II) and Cd(II) ions.

MATERIAL AND METHODS

Soil material, representing a grey-brown podzolic soil formed from loess (Orthic Luvisol) and a brown soil formed from heavy loam (Euthric Cambisol) (here called loess soil (A) and loamy soil (B)), was used in the studies. Samples were taken from accumulation horizon Ap (0-20 cm), air-dried, sieved with a sieve of 1 mm mesh diameter, and averaged. The main properties of the soils are given in Table 1.

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Table 1. Characteristics of studied soils

Soil	Granulometric composition (%, ϕ in mm)				$C_{org.}$ (%)	pH		Specific surface area (water vapour BET) (m^2 g^{-1})
	1-0.1	0.1-0.02	0.02-0.002	<0.002		H_2O	KCl	
Orthic Luvisol	1	63	27	9	2.13	4.8	4.3	24
Euthric Cambisol	29	19	34	18	1.70	6.2	5.9	59

The incubation experiment was done as follows: 0.05 kg soil samples were treated with solutions of $PtCl_4$ in the amount of 0.05 dm^3 in concentrations of 20, 40 and 200 mg Pt(IV) dm^{-3} as well as together with $PtCl_4$ solution and Pb(II) or Cd(II) salt solution in the form of $Pb(NO_3)_2$ or $CdCl_2$. The concentrations of the studied salts were 100 mg Pb(II) dm^{-3} or 50 mg Cd(II) dm^{-3} respectively (soil: solution ratio was 1:1). The samples, tightly closed in polypropylene beakers, were incubated at 5 and 20°C for 1, 2, 3, 4, 5 and 6 months.

When the incubation period was over, pH was measured using a microprocessor pH /Eh/°C meter with automatic temperature compensation.

Every sample, for which the incubation period had ended, was stirred, centrifuged and filtered off. The amounts of platinum ions obtained in the filtrate were measured by means of the voltamperometric method, with additional concentration, using the electrochemical analyzer EA9. Two series of measurements were taken for each sample. The results were elaborated statistically using the multifactor variance analysis. The factors included in the analysis were: ion (with or without lead and cadmium ions), concentration, time, and temperature. To evaluate the significance of differences between the means, Tukey's multiple test was applied, assuming a 5% error probability (parameter HSD).

RESULTS

As a result of the variance analysis, mean concentrations of Pt(IV) (mg dm^{-3}) were obtained for each of the considered values of concentration of Pt(IV), duration of experiment, temperature, and for each combination of solutions. The results are presented in Figs 1-5. The HSD parameter in the figures represents the smallest significant difference determining the importance of the experimental factors applied.

During loess soil treatment with solutions containing Pt(IV) ions, pH at 5°C changed from 3.93 to 5.65. At 20°C, the boundary values were 3.72 and 6.18. The range of pH changes after the addition of the solutions containing Pb(II) ions besides Pt(IV) ions into the loess soil at 5°C was 4.29-5.22, and at 20°C – 4.13-6.05. For the combinations with Cd(II) ions, the boundary values were 4.29 and 5.25 at the lower temperature, and 3.90 and 5.66 at the higher temperature (Fig. 1).

The pH values of the loamy soil treated with the solutions containing platinum ions and Pb(II) ions or Cd(II) ions were significantly higher than those obtained under the same conditions in the loess soil. After treating the loamy soil with Pt(IV) ion solutions, the boundary values of pH were 6.14 and 7.27 respectively, for the combination with Pb(II) ions 6.18 and 7.22, and with Cd(II) ions – 6.35 and 7.17 (Fig. 1).

While treating the loess soil with the solutions containing only Pt(IV) ions and with combination with Pb(II), pH changes were differentiated in individual periods but after 6 months these values were lower than after one month of incubation at both temperatures. In the loamy soil, a similar regularity was observed for the solutions containing only Pt(IV) ions and with Cd(II). However, pH changes were small - in the range of 0.08-0.30 unit - while in the loess soil they reached 1.76 units. In the loamy soil, for all the combinations used in the experiment, the largest pH values (about 7.1) were obtained after 3 months of incubation at 20°C.

As follows from the studies, the loess soil reaction changed in time and the most pronounced changes were observed at the higher temperature after using the solutions containing platinum ions with additional Pb(II) and Cd(II) ions. The temperature change caused an extensive differentiation in pH values at the beginning of the experiment, particularly after soil treatment with the solutions of lower platinum ions concentration. The introduction of larger amounts of Pt(IV) ions into the loess soil changed pH in most cases. The loamy soil reaction also changed in time, however, to a smaller extent than in the loess soil.

In both soils, at 5°C larger amounts of Pt(IV) ions were obtained in the filtrates. In the loess soil the amount of Pt(IV) ions was doubled, and in the loamy soil it was six times as large as at 20°C. In the loamy soil the amount of non-adsorbed platinum ions was significantly smaller compared with the loess soil for the temperatures used in the experiment (Fig. 2).

During the experiment, a similar regularity was found in both soils *ie* Pt(IV) ions were sorbed most strongly by the soil at the beginning of the experiment, after a month of using Pt(IV) ions solutions in all the combinations. At that time, in the loamy soil the Pt(IV) content obtained from the

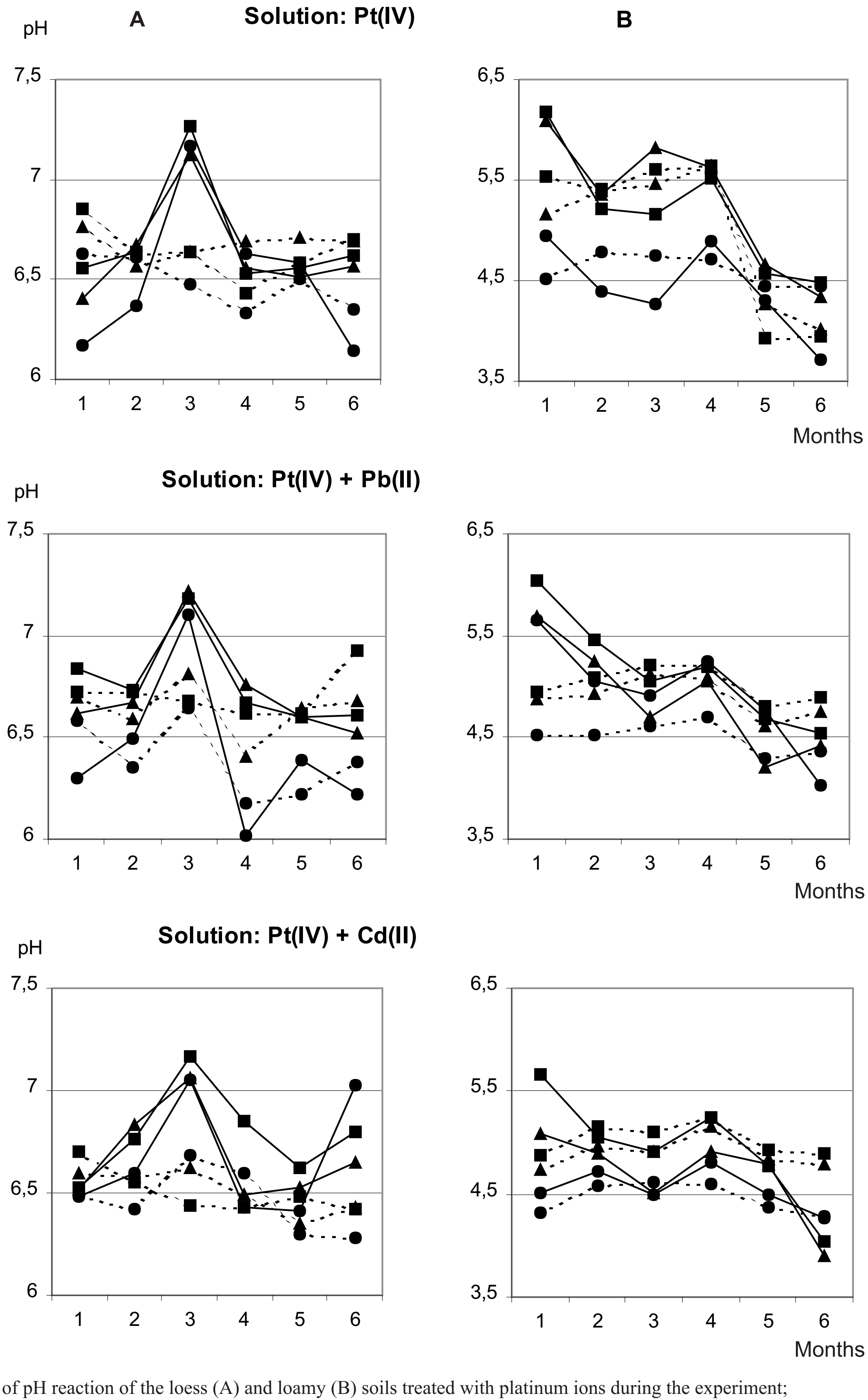

Fig. 1. Change of pH reaction of the loess (A) and loamy (B) soils treated with platinum ions during the experiment;
■ 20 mg Pt^{4+} dm^{-3} ▲ 40 mg Pt^{4+} dm^{-3} ● 200 mg Pt^{4+} dm^{-3} — 20°C - - - 5°C.

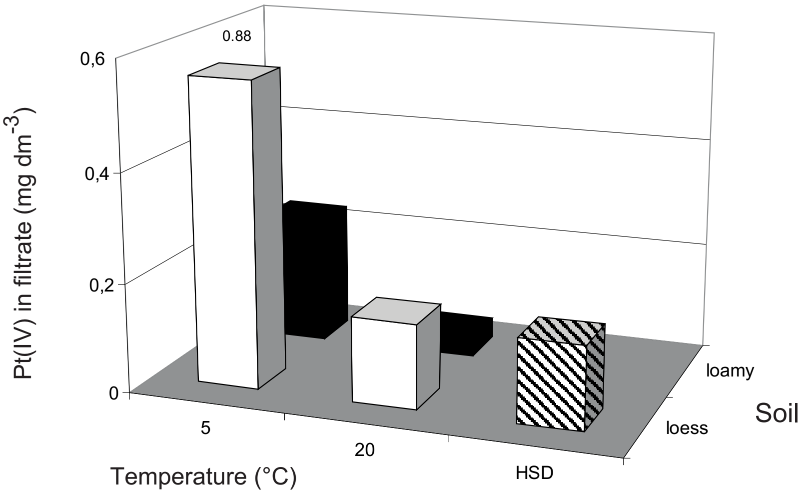

Fig. 2. Average amounts of Pt(IV) ions in the filtrates from the loess and loamy soils for two temperatures.

filtrate constituted only 30% of the amount obtained in the loess soil. Prolongation of incubation time in both soils did not result in significant changes of adsorbed Pt(IV) ions (Fig. 3).

Analysis of the concentration effect of Pt(IV) ions introduced into the soils showed that only the concentration 200 mg Pt(IV) dm^{-3} in all the combinations had a significant effect on the amount of platinum ions obtained in filtrates from both the loess and loamy soils. However, in the loamy soil the sorption of platinum ions was four times higher after the application of this concentration as compared with the loess soil (Fig. 4).

The largest amounts of Pt(IV) ions were obtained after treatment with the solutions containing additional Pb(II) and Cd(II) ions in the filtrates from both soils. In the loamy soil, in the presence of both ions, Pt(IV) ions sorption was similar, and in the loess soil the largest Pt(IV) sorption was observed in the presence of Pb(II) ions. As for the previous experimental factors, the amount of adsorbed platinum ions in the loess soil was significantly smaller than in the loamy soil (Fig. 5).

Platinum ions sorption was related to the same experimental factors in both the loess and the loamy soils, but the amount of adsorbed Pt(IV) ions was much larger in the loamy soil than in the loess soil *ie* 0.14 mg Pt(IV) dm^{-3} was obtained in the filtrates from the loamy soil and 0.52 mg Pt(IV) dm^{-3} from the loess soil.

Platinum forms minerals with sulphur and arsenic (PtS, $PtAs_2$), but also frequently accompanies deposits of nickel and copper, and jointly bonds with oxide minerals. Platinum occurs at oxidation states 2+ and 4+ and forms complexes with numerous anions as well as with organic compounds (Kabata-Pendias and Pandias, 1999). When introduced into loess and loamy soils in the form of Pt(IV) ions under the

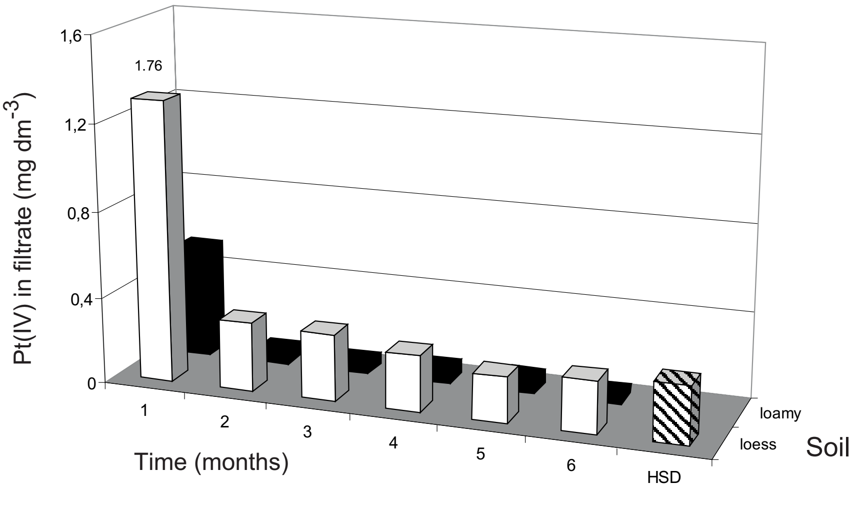

Fig. 3. Average amounts of Pt(IV) ions in the filtrates from the loess and loamy soils during the experiment.

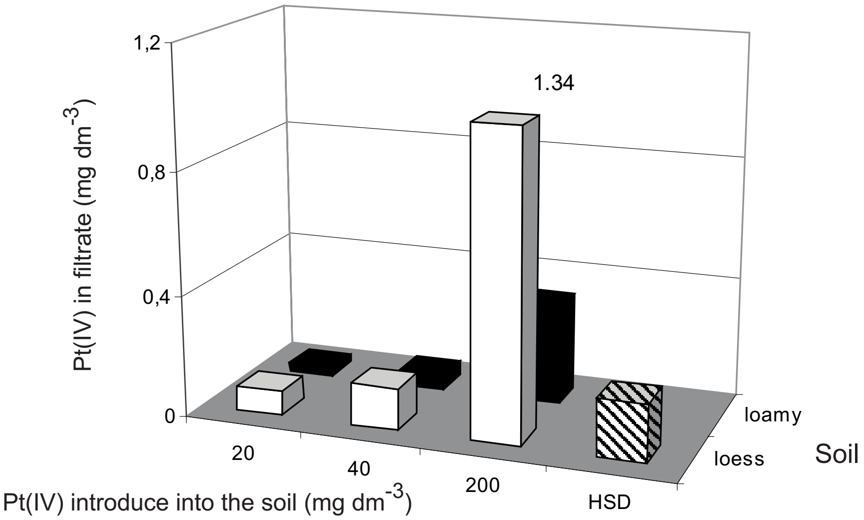

Fig. 4. Average amounts of Pt(IV) ions in the filtrates from the loess and loamy soils for vaious concentrations of Pt(IV) in solutions.

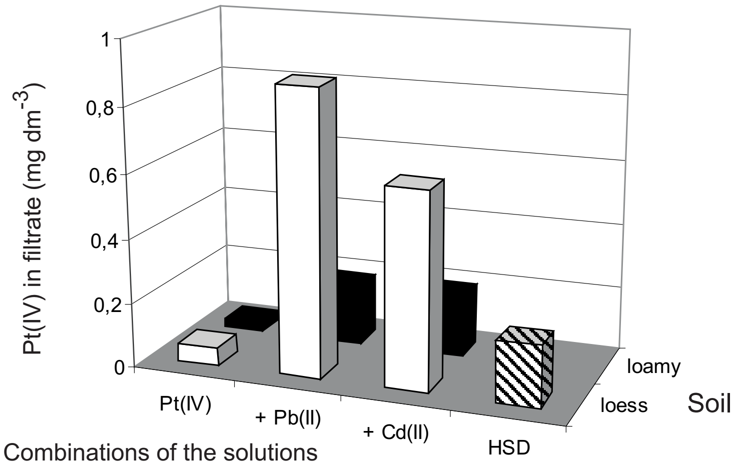

Fig. 5. Average amounts of Pt(IV) ions in the filtrates from the loess and loamy soils for individual combinations of solutions.

conditions of the experiment, it is adsorbed in significant amounts. As has been shown by earlier studies (Ballach, 1997; Ballach *et al*., 1999), phytotoxicity of platinum depends on the concentration of humic substance and clay minerals contents in the soil. The soil rich in those constituents, therefore, plays an important role in the immobilization of platinum (Verstraete *et al*., 1998) due to the formation of permanent complexes with humic acids or to sorption on the surface of clay minerals. Platinum fixed in the solid soil phase is unavailable to plants (Lusting *et al*., 1996). On the other hand, studies made by Wood (1990) show that humic substances (fulvic and humic acids) play significant role in the chemical transport of platinum metals, and thus also of platinum itself. Both the fulvic acids and other organic ligands (acetates, oxalates or phthalates) are responsible for increased solubility of platinum in water environments as compared to distilled water. Studies by Azaroul *et al*. (2001) showed that in the absence of strong ligands (Cl^-, CN^-) hydroxyl complexes of platinum play a significant role in controlling the behaviour of platinum in surface environments, *eg* in the soil, and therefore the mobility and transport of platinum can be controlled by means of the mechanisms of adsorption-desorption on oxides and hydroxides. One cannot also totally exclude the formation of colloidal particles or the reduction of platinum to insoluble forms. Any change in soil pH, oxidation-reduction potential, or the appearance of stronger complex-forming factors, *eg* EDTA, may cause ions formerly fixed to become available (Rauch and Morrison, 1999). Also, the presence of sulphur compounds cause an increase in the solubility of platinum in the soil environment through the formation of complex compounds (Wood, 1996). If platinum occurs in the soil in easily soluble forms, it is taken up by plants and accumulates mainly in the roots, which has been shown by studies on the water hyacinth *Eichhornia Crassipes* (Farago and Parson, 1994).

According to Sassani and Shock (1998), the solubility of platinum compounds is a function of pH, state of Pt oxidation, and the content of chlorides in geological formations. For pH>10 the dominant form is $Pt(OH)_{2(aq)}$, and for pH<4 - $PtCl_4^{2-}$. The temperature is a significant factor determining the stability of platinum compounds, too. According to those authors, chloride complexes of platinum can be more stable at lower temperatures, this could explain the lower sorption of platinum ions at 5°C in the soils used in present experiment.

Platinum ions were sorbed in the soils in lower amounts in the presence of lead and cadmium ions. This means that Pb(II) ions are characterized by high affinity to the loess soil. They were sorbed more strongly, probably replacing platinum ions. Therefore, lead ions are less mobile in the soil than platinum ions (Bojanowska, 2005). Similar results were obtained by Paszko (Paszko, 1998) in his studies, where lead cations were most strongly bound by the active centres of the soil.

The greater sorption of platinum in the presence of cadmium ions can be attributed to the higher mobility of cadmium ions, and thus to their notably lower affinity to the loess soil. In the loamy soil, the amount of platinum ions adsorbed in the presence of lead ions was similar to that in the presence of cadmium ions.

The study reported on herein indicate that under the conditions of the existing aeration (oxygenation) of the soils the mobility of ions can be represented by the following order: Pb < Pt < Cd.

CONCLUSIONS

The study showed that the sorption of platinum ions (IV) in the loess and loamy soil was related to temperature, concentration of platinum ions, duration of the experiment, and to the presence of lead and cadmium ions. However, following the impact of each of the factors of the experiment on Pt(IV) ions adsorption, more platinum ions (IV) were sorbed in the loamy soil as compared to the loess soil.

1. The amount of adsorbed Pt(IV) ions was related to the temperature. At the temperature of 5°C, in both the soils the amount of adsorbed platinum ions was lower than at 20°C.

2. The duration of incubation time of the experiment also had an effect on the amount of platinum ions sorbed in the soils. Longer contact time of soil and Pt(IV) ions resulted in greater sorption of Pt(IV) ions both in the loess soil and in the loamy soil.

3. In the experiment with solutions of various concentrations of platinum ions (20, 40 and 200 mg Pt(IV) dm^{-3}), the sorption of platinum ions was the lowest in the case of the solution with the highest concentration of Pt(IV) ions.

4. The amount of adsorbed Pt(IV) ions was also limited by the presence of Pb(II) and Cd(II) ions in both the soils under study.

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