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Electrokinetic Method for Purification of Soils Contaminated with Mercury(II) Compounds

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Abstract—A method of electrokinetic purification of soils contaminated with mercury compounds was developed. It was shown that $HgCl_3^-$, $HgCl_4^{-2}$, $HgBr_3^-$, $HgBr_4^{-2}$, and HgI_4^{-2} ions are the dominant mercury contaminants in the soil samples treated with aqueous solutions of NaCl, NaBr, and NaI extractants which form strong soluble complexes with mercury. The Russian commercial grade anion exchangers AV-17 and ANKS and cation exchanger KU-2 were used to remove mercury halide ions accumulated in the vicinity of the anode and cathode. The kinetics of sorption of anionic mercury complexes on the anion exchangers were investigated. A pilot device comprising replaceable ion-exchange cartridges for electrokinetic purification of soils was designed and fabricated. Two series of soil demercurization experiments using the pilot device and solutions of the complexing extractant agents NaCl and NaBr were carried out. It was shown that the soil sample with the initial contamination of 300 mg Hg(II)/kg could be purified up to 1.25 mg Hg(II)/kg within 30 days using the electrokinetic method and NaBr as extractant.

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INTRODUCTION

Inorganic mercury compounds are the most toxic environmental contaminants. They pose a serious environmental threat in the case of contamination of water reservoirs, soil, and biota as a whole. The high volatility, ability for transboundary transport, and diverse speciations allow mercury compounds to pass different barriers in biont bodies and exhibit an abnormally high environmental toxicity due to bioconcentration in trophic chains [1–3]. The environmental disaster in Canada in 1970 gave evidence to show that low mercury concentrations in water (not exceeding the MAC values), create, due to bioconcentration in trophic chains, dangerous or even lethal mercury concentrations in the higher consumer biomass.

In this connection purification of soil from mercury is the key task in ensuring chemical safety and environmental problem and environment enhancement [4]. In the present paper we present one of the approaches to solving this task.

Isolation and Neutralization of Mercury Compounds Extracted from Soil by Means of Electrokinetic Drainage

Mercury-containing wastes formed in soil and ground demercurization processes should be stored in special conditions because of the possible conversion of mercury compounds in a reductive medium into metallic mercury and into alkyl and dialkyl mercury in rigid anaerobic conditions [5]:

$$\mathrm{Hg(0) \leftrightarrow Hg(I) \leftrightarrow Hg(II) \leftrightarrow HgRCl \leftrightarrow HgR_2}.$$

Divalent mercury can exist in five forms: two cationic, one neutral (salt), and two ionic:

$$\mathrm{[Hg]^{+2} \leftrightarrow [HgCl]^{+} \leftrightarrow HgCl_2 \leftrightarrow [HgCl_3]^{-} \leftrightarrow [HgCl_4]^{-2}}.$$

The concentrations and their distribution, as well as existence of different mercury forms depend on the pH and redox potential of the medium, and the equilibria are complicated by precipitate formation in the presence of traces of sulfide and carbonate ions [6]. In this connection, disposal technologies of mercury-containing wastes envision pretreatment of mercury extracted from soil.

A newly developed technology for soil demercurization should meet the requirement to ensure either efficient isolation of toxic agents with their conversion into inactive forms resistant to biodegradation or efficient recycling to obtain a mercury-containing raw material.

Before disposal mercury-containing solid wastes which are difficult to recycle are isolated by immobilization by methods analogous those used for radioactive solid wastes (bituminization, cementation) or by the same methods with preliminary binding on vermiculite or ion exchangers selective to a target component.

The key task to be solved at the first stage of soil purification from mercury is to extract from soil as much mercury as possible, thus excluding its release to trophic chains; at the second stage the extracted toxic agent should be neutralized or isolated.

In the present paper we propose an electrokinetic method for mercury extraction from soil. In this method, applied electric field sets in motion mercury ions and simultaneously induces electrolysis of the soil solution with concentration of mercury-containing components in the near-electrode space: in the catholyte and/or anolyte region. It should be stressed that the diversity of ionic mercury species and their interconversions strongly complicate directed transport of mercury in the electric field. Mercury-containing compounds are accumulated in the catholyte or anolyte and should be immediately extracted and neutralized. The only efficient approach capable of meeting this requirement is provided by selective sorption via formation of stable mercury complexes. Sorption processes allow one to solve the principal tasks of soil demercurization: extraction of mercury and its compounds from drainage solutions using selective sorbents and extraction of mercury compounds from mercury-saturated sorbents or from draining solutions for the purpose of recycling of the extracted compounds as a mercury-containing raw material.

Each of these tasks makes its specific demands to the selectivity and sorption characteristics of sorbents to be used.

To choose appropriate sorbents and conditions for demercurization reactions, we have analyzed the equilibrium speciation of mercury halides in soils.

Dominant Mercury Halide Species in Soils

What mercury species form in soil depends on the type of the soil, its humidity, content of organic and inorganic complexing agents, ground water depth level, and human activity impact [7–9].

Mercury-containing wastewaters and soil solutions almost always contain chloride ions which are active complexing agents. As a result, the neutral molecules $HgCl_2$, cations $HgCl^+$, or anionic complexes $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ can be present in the solution. If wastewaters and soil solutions contain Hg(II) together with I^- or Br^- ions, the equilibrium composition of mercury complexes formed by reaction of Hg(II) will these halide ions will differ from that formed with chloride ions.

Published information on the composition of iodide and chloride anionic mercury complexes in dilute solutions is quite scarce, and, therefore, to identify mercury compounds in soil solutions we should initially determine the speciation of Hg(II) in soil.

To determine the dominating forms and charges of Hg(II) complexes in the soil solution, we calculated concentration distribution diagrams.

The distribution of mercury species and concentrations depends on the pH of the medium and the concentrations of chloride, bromide, and iodide ions in the soil solution. The equilibrium in a solution containing mercury halide species can be described by the equations of stepwise equilibrium reactions of formation of these species:

$$\begin{gathered}
[HgHal]^+ \leftrightarrow K_1\cdot[Hg^{+2}]\cdot[Hal^-],\\
[HgHal_2] \leftrightarrow K_2\cdot[Hg^{+2}]\cdot[Hal^-]^2,\\
[HgHal_3]^- \leftrightarrow K_3\cdot[Hg^{+2}]\cdot[Hal^-]^3,\\
[HgHal_4]^{-2} \leftrightarrow K_4\cdot[Hg^{+2}]\cdot[Hal^-]^4,
\end{gathered} \tag{1}$$

where K_1, K_2, K_3, and K_4 are equilibrium constants and Hal are Cl, Br, and I.

The equilibrium (dissociation or instability) constants of the complexes for reactions (1) are listed in Table 1 [10]. Comparison of the instability constants of Hg(II) chloride, bromide, and iodide complexes shows that the chloride complexes are less stable compared with the bromide and iodide complexes: In the case of chloride complexes, more free ions pass into solution, that with $[HgBr_4]^{-2}$ and $[HgI_4]^{-2}$. A complex dissociates if the concentration of one of its components decreases.

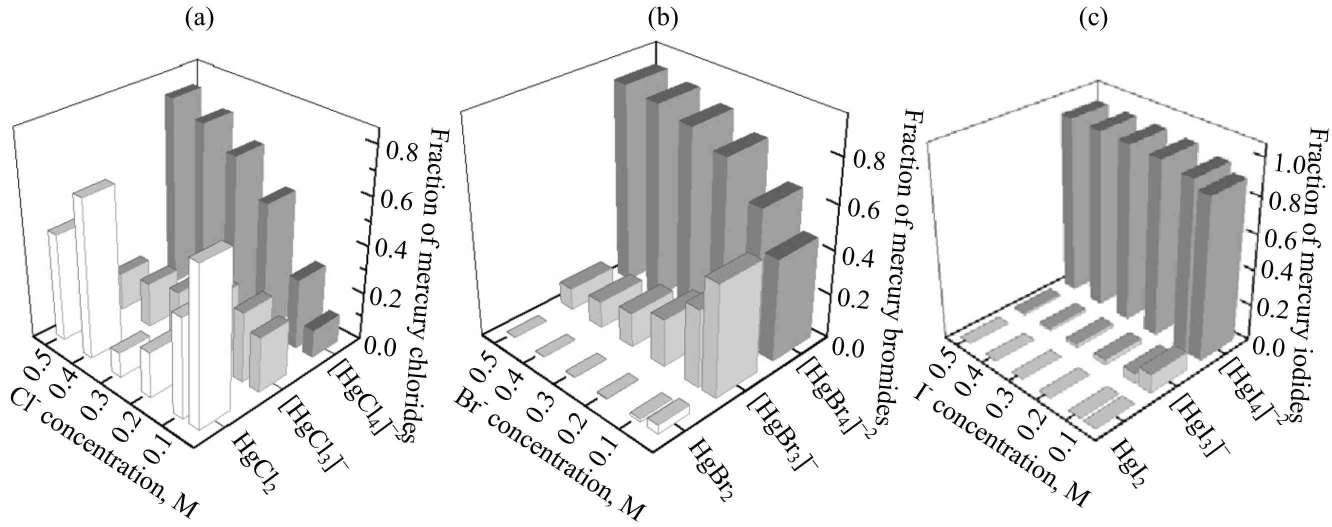

Fig. 1. Distribution diagrams of dominating mercury complexes as a function of the concentrations of (a) Cl^-, (b) Br^-, and (c) I^- ions.

In view of the absence of systematic research of the regularities of formation of different Hg(II) species, we performed a mathematical calculation of the concentration changes of different mercury species as a function the type and concentration of the accompanying halide ion (0.05–0.5 M). The calculation was based on the mass balance equations and the equations of formation of anionic Hg(II) complexes with the equilibrium constants listed in Table. 1. The calculation results are presented in Fig. 1. (As the fractions of Hg^{2+}, $HgCl^+$, $HgBr^+$, and HgI^+ ions are negligible compared with the fractions of other mercury halides, we don't show them in the diagrams in Fig. 1).

The concentration distribution diagrams show that at the Cl^- concentration of 0.05 M the dominating species in the solution are the neutral molecules $HgCl_2$ (65%). The fraction of the single charged anionic complexes $[HgCl_3]^-$ is no higher than 23%, and the fraction of the double charged anionic complexes $[HgCl_4]^{2-}$ is 12%. As the concentration of chloride ions in the solution increases to 0.1 M, the concentration of the anionic Hg(II) complexes increases to 58%, and, therewith, the total concentration of $[HgCl_3]^-$ and $[HgCl_4]^{-2}$ is higher compared with that of the neutral molecule $HgCl_2$.

A slightly different situation is observed, if dilute Hg(II) solutions contain Br^- and I^- ions in the same concentrations as Cl^- ions. Thus, the dominating species in Hg(II) solutions containing Br^- at a concentration of 0.05 M is $[HgBr_3]^-$ whose concentration decreases from 50% to 1% with increasing Br^- concentration, as well as $[HgBr_4]^{-2}$ whose concentration increases from 46% to 90%. The neutral molecules $HgBr_2$ are almost absent.

In solutions containing I^- ions, virtually no other species than the double charged anionic complex $[HgI_4]^{2-}$ was detected over the entire I^- concentration range (0.05–0.5 M).

The above-described changes in the composition of dominating Hg(II) species, depending on the type of the halide ion and its concentration should be taken into account in selecting an ion-exchange resin for extraction of toxic mercury compounds from soil solutions.

Sorbents for Extraction of Mercury Compounds from Draining Solutions

The Russian commercial anion exchangers AV-17, AN-221, AN-511, and ANKS (Technical Specifications 6-05221-1447-87) (Table 2) were tested as candidate sorbents for extraction of mercury compounds from soil solutions. These anion exchangers have similarly structured polymer matrices but different functional groups.

The AV-17 anion exchanger contains a functionality derived from trimethylamine (quaternary amino groups), the functional groups in the AN-221 anion exchanger are derived from ethyleneamine (i.e. primary and secondary amino groups); and the AN-511 anion exchanger contains an analogous amino group

Table 1. Equilibrium stepwise formation constants of mercury halide complexes

Addends	Ligand central ion	log K_1	log K_2	log K_3	log K_4
Cl^-	Hg^{+2}	6.74	6.48	0.85	1.00
Br^-		9.05	8.28	2.41	1.26
I^-		12.87	10.95	3.78	2.23

from diethylenetriamine but has a higher exchange capacity for chloride ions. The ANKS ion exchanger was prepared by the modification of the AN-221 anion exchanger by SH groups.

According to preliminary results, the AV-17 and ANKS anion exchangers showed enhanced selectivity of extraction of Hg(II), Pb(IV), and As(III) ions from industrial wastewaters [11]. These anion exchangers ensured the highest degree of purification from these elements (to MAC_{water} 0.001–0.005 mg/L). The sorption by these anion exchangers is underlain by Hg(II) reaction with amino groups to form mercury complexes.

Sorption Kinetics of Anionic Mercury Complexes

We studied the kinetics of sorption of the mercury halide anionic complexes $[HgBr_4]^{2-}$, $[HgBr_3]^-$, $[HgI_4]^{2-}$, $[HgI_3]^-$, $[HgCl_4]^{2-}$, and $[HgCl_3]^-$ on the macroporous ion exchangers AV-17 and ANKS. Experiments were performed in a temperature-controlled reactor with a stirrer (rotational speed 60 rpm) at 25, 35, and 45°C. The reactor was loaded with an ion exchanger (0.5±0.05 g) and 200 ml of a 0.1 N solution of NaCl (NaBr and NaI) containing 3×10^{-3} mol/L of Hg(II). The concentration of Hg(II) was determined by photometric titration with crystal violet dye on a Spekol-221 instrument (λ 605 nm, *l* 10 mm). The error in the concentration measurements was ±5% [12].

The degree of filling $F(t)$ of an ion exchanger with anionic Hg(II) complexes was calculated by the formula:

$$F(t) = C(t)/C_e,$$

where $C(t)$ is the concentration of Hg(II) in the ion exchanger phase at time t and C_e, equilibrium capacity of the ion exchanger at given conditions (at the initial concentration of Hg(II) and experimental temperature).

In solutions with comparable ionic strengths, the dominant mercury species is $[Hg(Hal)_4]^{2-}$. However, in view of the diversity of Hg(II) species, the sorption process can be complicated or follow a formal diffusion equation that describes the diffusion of the neutral molecule $Hg(Hal)_2$ into ion exchanger granules.

Figure 2 shows the experimental kinetic curves of sorption of anionic Hg(II) complexes on the AV-17 and ANKS ion exchangers. A minor effect of external diffusion of the kinetics of sorption on macroporous ion exchangers at high stirring speeds in a limited volume was noted. A characteristic feature of this process is that its rate increases with increasing rate of motion of the external solution due to increasing external mass-transfer coefficient. Sorption processes occurred in a mixed region, where the contribution of internal diffusion and chemical reaction were comparable.

The curves in Fig. 2 show that the estimated times of extraction of mercury halide species from solutions with the AV-17 and ANKS anion exchangers at room temperature (no longer than a few hours) are much shorter than the usual times of drainage soil purification (tens of days). Therewith, the equilibrium ion-exchange capacities of the sorbents were used by 70–90%. Consequently, the ion extraction process is limiting, and the chosen sorption materials (AV-17 and ANKS) can be used for isolation and neutralization of mercury compounds accumulated in the vicinity of the anode and cathode.

Table 2. Physicochemical characteristics of ion exchangers[a]

Brand	Ion-exchange group	Static volume capacity by 0.1 N HCl, mmol/g	Specific surface area, m^2/g
AV-17	$-N^+(CH_3)_3Cl^-$	3.7	32
AN-221	$-NHC_2H_4NH_2$	4.35	28
AN-511	$-NHC_2H_4NHC_2H_4NH_2$	6.3	20
ANKS[b]	$-CH_2N(C_2H_4SH)C_2H_4N(C_2H_4SH)_2$	3.9	24

[a] All ion exchangers were used in the OH form. [b] The N/S molar ratio in the ANKS ion exchanger is 2.5/2.

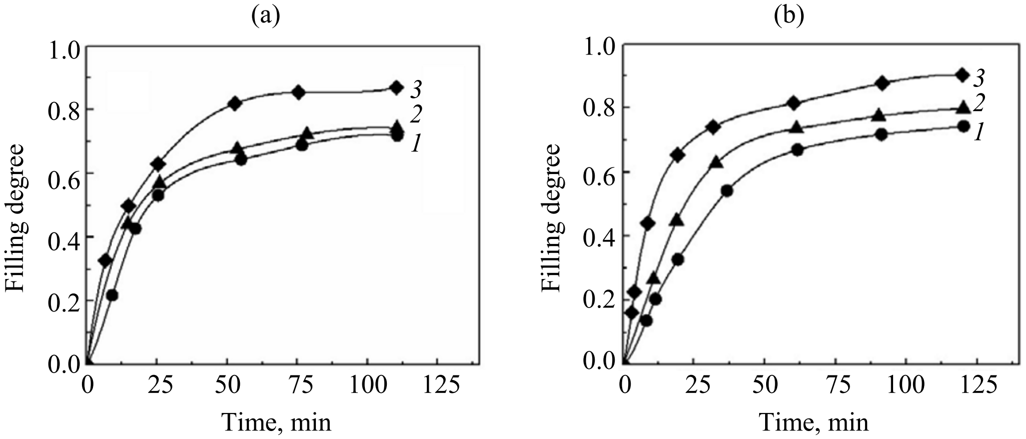

Fig. 2. Kinetic curves of sorption on (a) AV-17 and (b) ANKS ion exchangers of anionic Hg(II) complexes from aqueous solutions of mercury halide salts.

Moreover, our previous research on the sorption of all the three tetrahalide complexes [10] revealed preference for tetrabromide complexes by the key equilibrium and kinetic parameters. Thus, tetrabromide complexes showed higher ion-exchange constants (by 20–30%) and limiting surface and volume partition coefficients (up to 10 times) on the studied sorbents.

Technology of Soil Purification from Mercury by the Electrokinetic Method with Sorption Cartridges

Based on the results of study of the equilibrium and kinetics of sorption of mercury complexes we developed a technology for soil and water purification from mercury-containing compounds and fabricated a pilot electrokinetic device with sorption cartridges.

The pilot drainage device is constructed as a rectangular box (width 20 cm, length 30 cm) with electrodes (anode and cathode) on both sides (Fig. 3) and an insert on the bottom. The insert forms two wells for water collection. The near-electrode spaces are separated from the working space by semipermeable partitions that enclose the anolyte and catholyte compartments. The anolyte compartment is filled with a sorbent for anionic complexes, in particular, the AV-17 or ANKS anion exchangers, and the catholyte compartment is filled with a sorbent for cationic mercury species, for example the KU-2 cation exchanger.

The device allows treatment of fully wet soils (the water level is maintained constant, water covers the insert). The dimensions of the working compartment for the soils to be treated is 22 × 6 × 20 cm^3, the thickness of the soil layer in the working compartment is 6 cm, and the soil batch volume is 2.64 L. The dimensions of the near-electrode compartment with sorbent are 4 × 8 × 20 cm^3, and the ion exchanger batch volumes are 0.64 L.

Operational conditions of the device filled with a 1% NaCl solution: voltage 13 V, current density 0.2 A/m^2, electrode–electrode distance ~22 cm; continuous operation regime.

Operational conditions of the device filled with a 1% NaBr solution: voltage 40 V, current density 0.5 A/m^2 electrode–electrode distance ~22 cm; continuous operation regime.

The sorbent with accumulated mercury can be either taken out and regenerated or used as a raw material at a specialized mercury production facility.

A tube reaching the bottom of the compartment is used to withdraw the purified draining solution which can be further discharged (if its mercury level does not exceed the $MAC_{discharge}$) or can be recycled for washing a durty zone.

The optimal operational regimes of the device are as follows.

(1) An acidified (to pH 2–3) draining solution from the anolyte compartment is pumped through a bypass line to the zone before the catholyte compartment (on the left of the partition of the catholyte compartment). Transfer of the solutions from the anolyte compartment to this zone prevents precipitation of hydroxy complexes and allows efficient extraction of mercury and its active transport as anionic complexes to the anode. This approach prevents spreading of mercury pollution in area and depth.

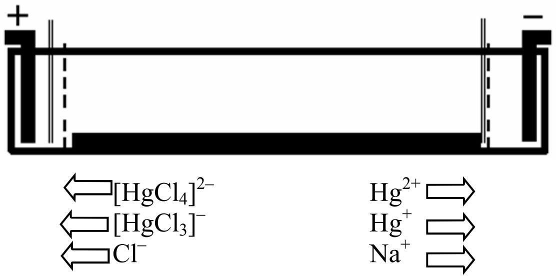

Fig. 3. Schematics of the electrokinetic drainage device for soil demercurization.

The method can also be used when costly or toxic agents are added into the draining solution as is the case of the iodide system, as well as for washing soil with sea or mineralized water containing chloride and bromide ions.

(2) If the solution from the sorbent-filled anolyte compartment is purified to $MAC_{discharge}$ levels, it can be discharged to the environment or, to avoid excessive soil salinization, recycled.

Performance Study of the Pilot Drainage Plant

As the soil to be purified, in our experiments we used coarse river sand (Table 3) contaminated with mercury (300 mg/kg). The residual contamination level should be lower than the MAC in agricultural soils (MAC_{soil} 2.1 mg/kg).

High degrees of purification are provided by costly draining solutions with complex compositions. According to published data, the iodide system showed the best results for mercury extraction from soil. However, we found that the bromide system offers essential kinetic advantages: The sorption of tetrabromide complexes on mercury ion exchangers featured the best equilibrium and kinetic parameters (the highest ion-exchange constants, limiting partition and internal diffusion coefficients).

Table 3. Characteristics of the soil sample

Soil characteristics	Soil	Water in soil
Density, kg/dm^3	2.7	–
Relative humidity, %	20	–
Thickness of soil sample, cm	6	–
Weight, kg	9.72	1.62
Volume, L	3.6	–
Mercury concentration, mg/kg		
initial	300	1800
final	2.1	12.6
Amount of mercury (in water), g	–	2.916

Table 4 lists selected characteristic of the system of complexing agents forming tetrahalide complexes at the mercury concentration of 300 mg/kg, total soil weight 9.72 kg, and humidity 20%. As seen, the final concentrations in the soil solution for different halogens span the range 0.61–1.57%.

The average degree of purification was determined using three samples of soil water, taken at the entrance of the zone (after the anolyte partition), in the middle of the working zone, and at the exit of the zone (before the catholyte partition).

The demercurization process was performed in two variants (Variant 1 and Variant 2). The resulting data are presented in Fig. 4. A time dependence of residual mercury contamination C_{res} and purification degree d were determined. The δ value was calculated by the formula:

$$\delta = \frac{C_{init} - C_{res}}{C_{init}} \times 100\%,$$

where C_{init} is the initial concentration of mercury in soil (in our experiments, 300 mg/kg).

In Variant 1, to form mercury complexes we used mercury chloride (1.2 g of anhydrous NaCl per 1 g of mercury; the NaCl concentration in the soil solution, estimated per 9.72 g of soil, is about 0.7%). The bypass line was not connected. Mercurization was performed at a voltage of 13 V and an initial current density of 0.2 A/m^2.

The $C_{res}(t)$ dependences in Fig. 4 are well fitted by descending exponents (the part of the exponent, corresponding to the demercurization time 1–30 days and shown in Fig. 4b is close to a straight line).

The Variant 1 regime does not allow purification to the MAC_{soil} level within a reasonable time period. The

Table 4. Characteristics of complexing systems

Halogen in NaHal	Consumption of NaHal, g/g Hg	Concentration in soil solution, %	Hal : Hg (mol)
Cl	1.2	0.61	4.00
Br	2.1	1.08	4.00
I	3.0	1.57	4.00

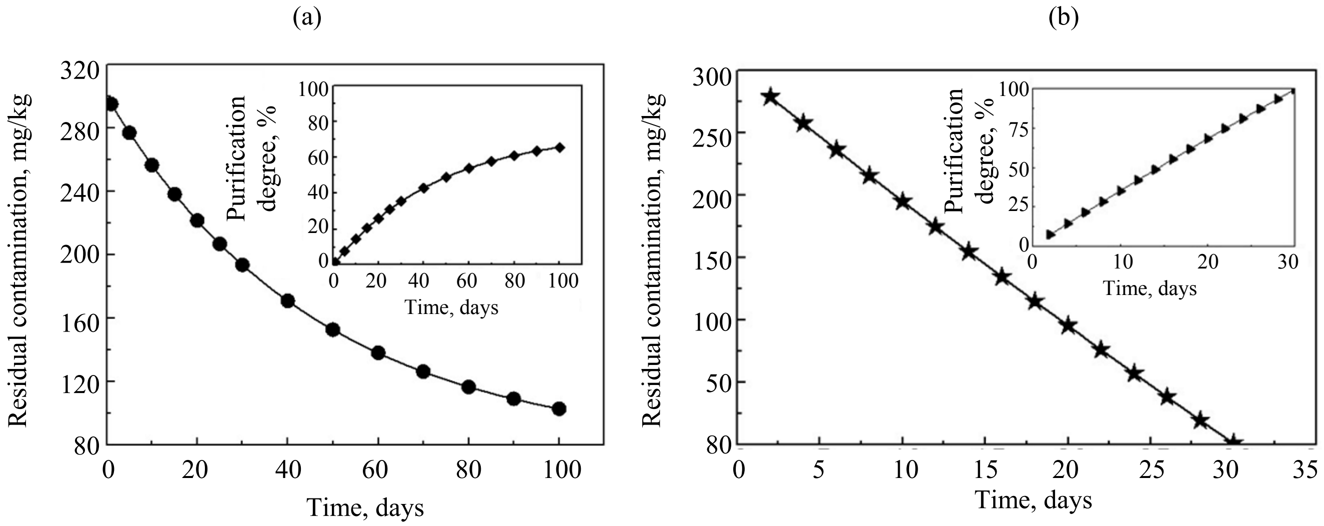

Fig. 4. Dependences of the residual contamination of soil with mercury and the purification degree on time. Complexing agent: (a) NaCl (Variant 1) and (b) NaBr (Variant 2).

average purification rate varies from 0.41 to 0.26 cm/day. The maximum purification degrees within 30 and 100 days are 35.5% and 65%, respectively.

In view of the fact that Variant 1 with chloride mercury complexes was found not to provide efficient demercurization, we chose a more efficient Variant 2 with the bromide system and a connected bypass line.

In Variant 2, to form mercury complexes we used sodium bromide (2.2 g of anhydrous NaBr per 1 g of mercury; the NaBr concentration in the soil solution, estimated per 9.72 g of soil, is about 1.1%). The bypass line was connected, recycle rate 2 mL/min. Mercurization was performed at a voltage of 40 V and an initial current density of 0.5 A/m^2.

Contaminated soil is purified by almost 100% within 30 days. The estimated power consumption for demercurization is fairly high (48 kW h/m^3 or 59.3 kW h/kg mercury), but the actual monthly power consumption of the device was 0.173 kW h.

Thus, the second variant of demercurization can be proposed as the basis for a design of an electrical drainage technology for soil demercurization.

CONCLUSIONS

The developed technology for the purification of soil from Hg(II) compounds, based on electrokinetic drainage and ion-exchange sorption, makes it possible to purify soil with the initial contamination 300 mg/kg to levels lower than the MAC$_{\text{soil}}$ (up to 1.25 mg/kg). The technology can be implemented in hardware as an electrical drainage device.

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