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Adsorption treatment of sewage sludge from heavy metals

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ABSTRACT: Introduction. Because of urban development the volume of municipal and industrial wastewater are growing. Along with them the amount of sewage sludge (SS) also increases. Millions of tons of SS are currently accumulated on the territory of the Russian Federation and contain various pollutants, including heavy metals (HM). In this regard, the search for effective methods of SS treatment from HM is an urgent problem. The main methods of SS treatment are drying, dehydration, thermal methods, UV and microwave wave treatment. These kinds of disinfection eliminates many pathogenic microorganisms, but they are quite expensive and not effective against HM. Reagent methods include SS disinfection with quicklime (CaO). However, decontamination requires large doses (up to 30%) and it is also ineffective against HM. Humic-mineral reagent are more effective, they are based on crushed caustobiolites, their cleaning capacity from HM is 19–87%. **Methods and materials.** The authors have previously shown the effectiveness of wastewater treatment from HM using sorbents based on dolomite, quartzite, and waste from mining and processing plants. Therefore, a method for SS treatment from HM using sorbents based on dolomite, humates, and CS containing $CaCO_3$ and humic compounds was proposed. In this regard, a method was proposed for SS treatment from HM using three types of sorbents based on: 1) waste of thermal power plants (TPP) – conditioned sludge (CS) containing $CaCO_3$ up to 68% and humic compounds up to 12% – sorbent 1 (S1); 2) dolomite – Mg and Ca carbonate in a composition with sodium humate (25%)– sorbent 2 (S2); 3) modified dolomite with sodium humate (1%) – sorbent 3 (S3). **Results and discussion.** In laboratory experiments, the cleaning capacity of SS was studied using a dolomite-based sorbent modified with humate (1%). In field tests, a decrease in the concentration of HM in SS was studied with the use of sorbents based on CS and the complex sorbent dolomite-humate (75:25). The cleaning capacity of SS from HM increases in the series: sorbents based on waste from TPP – CS containing $CaCO_3$ and humates (cleaning capacity E = 4.8–48.6% for dried SS and 29.3–53.3% for dehydrated SS) < sorbent based on a composition of dolomite with humate (E = 65.1–92.1% for dried and 56.6–89.4% for dehydrated SS) < a dolomite-based sorbent modified with humate (E = 90.8–99.9%). **Conclusions.** The maximum cleaning capacity is shown by a dolomite-based sorbent coated with a nano- and micro- sized layer of sodium humate.

KEYWORDS: sewage sludge treatment, sorbents, heavy metals, dolomite, humate, conditioned sludge.

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INTRODUCTION

Along with the development of cities and industrial centers, the volume of municipal and industrial wastewater is growing. Waste materials generated after wastewater treatment negatively affect the environment and the city's population.

Millions of tons of sewage sludge (SS) are currently accumulated on the territory of the Russian Federation. Most of its are located on the drying beds that are not equipped with waterproofing and the SS disposal mainly does not meet environmental requirements and standards accepted in the world. Accumulating near treatment facilities, SS pollute nearby territories, sur-

face water and groundwater. In this regard, the search for effective methods of SS treatment and disposal is an urgent problem.

SS contain significant amounts of heavy metals (HM), which are removed by various methods [1–8], including adsorption [9–14].

Primary treatment of SS is aimed at reducing weight, volume and disposal costs, as well as to reduce potential risks to human health during its disposal.

Sludge drying beds provide the simplest method of dewatering. Its humidity can be reduced to 75–80%. Vacuum filters are most widely used for mechanical dewatering.

The main methods of cleaning SS include thermal methods, UV and microwave wave treatment. These kinds of disinfection eliminates many or all pathogenic microorganisms, but they are quite expensive and not effective against HM.

Reagent methods include SS disinfection with quicklime (CaO). However, decontamination requires large doses (up to 30%) and it is ineffective against HM [15].

It is known that humates are good complexing agents of HM. It binds them into stable complexes and converting into fixed water-insoluble forms [16–17].

In the paper [16] to reduce the concentration of HM in polluted soils the authors used a humic-mineral reagent based on crushed caustobiolites obtained by mixing brown or oxidized coal with KOH or NaOH. This reagent contains a significant amount of humic acidsand the authors [16] found that the humic reagent reduces the concentration of HM in doses of 1–5% by weight in relation to the mass of soils contaminated with HM (Zn, Mn, Sr, Ni, Co, Cu, Pb, Cd), but not effectively enough (table 1).

It is known that wastes from thermal power plants (TPP) – conditioned sludge (CS) are used as sorbents, which mainly consist of $CaCO_3$ and contain up to 12% humates [18–19]. Such sorbents can be used for waste water treatment from petroleum products and HM.

In our works [9, 10, 17, 20–22], it was shown that sorbents based on dolomite, quartzite, and waste from mining and processing plants are highly effective in treating wastewater from HM.

Therefore, we have proposed a comprehensive method for cleaning SS from HM using sorbents based on dolomite, humates, and CS containing $CaCO_3$ and humic compounds.

METHODS AND MATERIALS

The research object is SS – a solid fraction, that is formed as a result of the wastewater treatment process and consists of organic and mineral substances, including HM in concentrations significantly exceeding the maximum permissible standards (MPS).

As materials for the preparation of sorbents were used:

- conditioned sludge, which mainly consist of $CaCO_3$ (up to 68%) – sorbent 1 (S1);
- composite sorbent based on dolomite and humate (25%)– sorbent 2 (S2);
- dolomite with nano- and micro-sized layers of humates deposited on its surface (modified dolomite) – sorbent 3 (S3).

Table 1
Effectiveness of soil sanitation with humic-mineral reagent

Heavy metal (HM)	Average concentration of HM in the soil before sanitation, mg/kg	Average concentration of HM in the soil after sanitation, mg/kg	Effectiveness of soil sanitation, %
Zink	25	10.1	60
Manganese	7.7	6.24	19
Strontium	45.6	5.78	87
Nickel	9.6	2.7	72
Cobalt	9.3	3.66	61
Chrome	23.7	5.38	77
Copper	4.3	2.46	43
Lead	34.8	9.32	73
Arsenic	12	1.76	85
Vanadium	8.4	6.18	26
Antimony	0.7	0.268	62
Tin	12.2	5.28	57
Cadmium	0.99	0.338	66

Table 2
Chemical composition of dolomite

№	Component	Component content, % by weight.	№	Component	Component content, % by weight.
1	CaO	29.2	10	As	<0.002
2	SiO_2	2.97	11	Pb	<0.005
3	Fe_2O_3	0.44	12	Mn	0.021
4	Al_2O3	0.45	13	Co	<0.005
5	MgO	21.1	14	Cu	<0.005
6	K_2O	0.27	15	Mo	0.0022
7	Na_2O	0.041	16	Cd	<0.001
8	S	<0.005	17	Cr	<0.005
9	F	<0.1	18	Hg	<0.00001

The studies were performed using x-ray fluorescence analysis (XRF) on a VRA-30 spectrometer and inductively coupled plasma atomic emission spectrometry (ICP-AES) on an ICPE-9000 spectrophotometer with a spectral range of 167–800 nm and a detection limit of 1 mg/kg.

The chemical composition of S1 (%): SiO_2 – 0–4.9; $Fe(OH)_3$ – 5.8–7.1; $CaSO_4 \cdot 2H_2O$ – 3–9.5; $CaCO_3$ – 62.8–68.2; $MgCO_3$ – 3.9–6.6; organic matter – 5.2–8.9.

The concentration of HM cations (% of weight): Cu^{2+} – 0.04–0.014; Ni^{+2} – 0.008 ± 0.003; Zn^{2+} – 0.033–0.013; Mn^{2+} – 1.05–0.407; Cr^{3+} – 0.001 ± 0.0003; Pb^{2+} – 0.002 ± 0.0003; Cd^{2+} – 0.22 ± 0.08.

Dolomite is a sedimentary carbonate rock of white or dark gray color. It mainly consist of the Ca and Mg carbonates class mineral. The dolomite used in the work in the form of dolomite chips (DC) – waste product of dolomite processing [23–24], the chemical composition of which is shown in table 2.

Laboratory experiments were carried out using S3, that containing 1% sodium humate deposited with a layer 200 nm – 50 microns thick [16]. 5 g of sorbent was added per 100 g of SS and actively mixed for 5 days at room temperature. As a result of this treatment, the concentrations of all the studied HM decreased to values below the MPS in the soil.

Samples of SS from the municipal unitary enterprise «Ufavodokanal» were used in the experiments. The SS previously were dewatered to a humidity of 27% at a temperature of ~150°C.

HM concentrations were determined using the ICP-AES method using an ICPE-9000 spectrophotometer.

Table 3
Results of laboratory experiments and calculation of the effectiveness of reducing the concentration of HM after SS treatment with S3

Heavy metal (HM)	HM concentration in SS before cleaning, mg/kg	The limit values for HM in the soil, mg/kg	HM concentration in SS after cleaning, mg/kg	Efficiency (E, %)
Lead	550	130.0	2.3 ± 0.7	90.1
Cadmium	4.32	2.0	0.11 ± 0.03	97.4
Zink	1000	220	0.96 ± 0.29	99.9
Copper	226	132.0	0.22 ± 0.07	99.9
Chrome	130	6	4.1 ± 1.2	96.8
Nickel	205	80.0	1.5 ± 0.4	99.3
Arsenic	2.7	2.0	0.032 ± 0.010	98.8

The effectiveness of reducing the concentration of HM in SS was calculated using the formula:

$$E = (C_0 - C_t)/C_0 \cdot 100\%,$$

where C_0, C_t – are the values of HM concentrations in SS before and after SS purification, respectively.

RESULTS AND DISCUSSIONS

We have conducted studies of sorption treatment of SS from HM in laboratory and field conditions using various types of sorbents.

The results of laboratory experiments using S3 are shown in table 3.

According to table 3, a high efficiency of reducing the concentration of HM in the SS samples was achieved and mainly amounted to 97–99.9%, only for Pb the efficiency was 90.8%.

In order to bring the experiment conditions as close as possible to the actual conditions for processing SS, field tests were conducted. The technological platform has a waterproofing base and is equipped with a drainage ditch.

Field tests were conducted in several stages:

– preparation temporary composting field for the receiving of SS;
– receiving SS;

Two types of SS samples from the municipal unitary enterprise «Ufavodokanal» were used: dried to a humidity of 36% at a temperature of 20–30°C (dried SS) and dehydrated to a humidity of 27% at a temperature of 150°C (dehydrated SS).

Table 4

Results of field tests and calculation of the effectiveness of reducing the concentration of HM after SS treatment with a S1

Heavy metal (HM)	HM concentration in SS, mg/kg					
	Sample № 6 of dried SS		Efficiency (E, %)	Samples № 2 of dehydrated SS		Efficiency (E, %)
	before cleaning	after cleaning		before cleaning	after cleaning	
Copper	226 ± 57	215 ± 54	4.8	158 ± 40	108 ± 23	31.6
Zink	1000 ± 250	630 ± 160	37.0	430 ± 110	304 ± 64	29.3
Iron	13900 ± 3500	18000 ± 5000	–	11985 ± 3020	–	–
Calcium	41000 ± 10000	34000 ± 9000	17.0	16000 ± 4000	41000 ± 10000	–
Manganese	560 ± 140	320 ± 80	42.8	300 ± 80	–	–
Nilel	79 ± 20	60 ± 15	24.0	60 ± 15	28 ± 8	53.3
Cadmium	14.0 ± 3.5	7.2 ± 2.3	48.6	16.0 ± 4.0	10.0	37.5
Lead	25.0 ± 6.2	14 ± 4.0	44.0	–	–	–

Table 5

Results of field tests and calculation of the effectiveness of reducing the concentration of HM after treatment of SS with a S2

Heavy metal (HM)	HM concentration in SS, mg/kg					
	Sample № 6 of dried SS		Efficiency (E, %)	Samples № 2 of dehydrated SS		Efficiency (E, %)
	before cleaning	after cleaning		before cleaning	after cleaning	
Copper	226 ± 57	79 ± 20	65.1	158 ± 40	38 ± 9.5	75.9
Zink	1000 ± 250	114 ± 28	88.6	430 ± 108	125 ± 32	70.9
Nikel	79 ± 20	23.3 ± 5.8	70.5	60 ± 15	26.1 ± 5.0	56.6
Cadmium	14 ± 4.2	1.1 ± 0.2	92.1	16 ± 4.0	1.7 ± 4.2	89.4
Lead	89 ± 22	67 ± 16	24.7	14 ± 3.5	6.2 ± 1.6	52.0
Arsenic	2.7 ± 0.7	1.5 ± 0.4	44.4	2.7 ± 6.7	1.7 ± 4.2	30.8

– treatment of S1 and S2: mixing SS with sorbents 3–4 times within 4–5 days;
– sampling of treated SS and determination of HM concentrations in them by the ICR-AES method (table 4).

According to table 4, the using of S1 reduces the content of Zn, Mn, and Ni, but increases the concentrations of Fe and Ca and generally does not show high efficiency (4.8–48.6% for dried SS and 29.3–53.3 % for dehydrated SS). The concentration of Fe and Ca increases due to their presence in the CS.

Table 5 shows the results of field tests using a S2.

The efficiency of SS treatment using a S2 sorbent from Zn, Cu, Ni, Cd at room temperature is 65.1–92.1% for dried sludge and 56.6–89.4% for dehydrated sludge, for Pb and As – 24.7–44.4% and 52.0–30.8%, respectively (table 5).

Thus, comparing the results of tables 4 and 5, sorbents based on the composition of dolomite and humate showed higher efficiency of SS treatment than sorbents based on CS.

It should be noted that the efficiency of SS treatment with S2 and S3 decreases in the field experiments that in laboratory experiments, despite the fact that the humate concentration in the S3 was 1%, and in the S2 – 25% in relation to dolomite. This may be due to less efficient mixing of the S2 with SS in the field conditions. The relative efficiency of sorbents in the process of SS treatment from heavy metals increases in the series: S1<S2<S3.

CONCLUSIONS

Laboratory and field experiments were carried out to study the efficiency of SS treatment with sorbents based on waste from TPP and humic sorbents (based on dolomite and sodium humates) from heavy metals – Cu, Zn, Ni, Cd, Pb, As, Cr.

It was found that the efficiency of treatment increases in the following series: sorbents based on waste from TPP – CS (containing $CaCO_3$ and humates – treatment efficiency E = 4.8–48.6% for dried SS and 29.3–53.3% for dehydrated SS) < sorbent based on a composition of dolomite with humate (25% sodium humate, E = 65.1–92.1% for dried SS and 56.6–89.4% for dehydrated SS) < sorbent based on modified dolomite (1%, layer 200 nm – 50 microns, E = 90.8–99.9%).

A method for treatment of SS at water utilities and industrial enterprises based on humic sorbents is proposed.

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