Principles of Municipal Sewage Sludge Bioconversion into Biomineral Fertilizer

K. V. Kalinichenko, G. N. Nikovskaya

Abstract—The efficiency of heavy metals removal from sewage sludge in bioleaching processes with heterotrophic, chemoautotrophic (sulphur-oxidizing) sludge cenoses and chemical leaching (in distilled water, weakly acidic or alkaline medium) was compared. The efficacy of heavy metals removal from sewage sludge varies from 83 % (Zn) up to 14 % (Cr) and follows the order: Zn > Mn > Cu> Ni > Co > Pb > Cr. The advantages of metals bioleaching process at heterotrophic metabolism were shown. A new process for bioconversation of sewage sludge into fertilizer at middle temperatures after partial heavy metals removal was developed. This process is based on enhancing vital ability of heterotrophic microorganisms by adding easily metabolized nutrients and synthesis of metabolites by growing sludge cenoses. These metabolites possess the properties of heavy metals extractants and flocculants which provide the enhancement of sludge flocks sedimentation. The process results in biomineral fertilizer of prolonged action with immobilized sludge bioelements. The fertilizer satisfies the EU limits for the sewage sludge of agricultural utilization. High efficiency of the biomineral fertilizer obtained has been demonstrated in vegetation

Keywords—Fertilizer, heavy metals, leaching, sewage sludge.

I. INTRODUCTION

NE of the urgent contemporary problems is an utilization of contaminated with heavy metals sewage sludges produced in large quantities as a result of widespread biological treatment of municipal wastewater [1]-[3]. They are highly concentrated stable suspensions of biological cells, their metabolites and heavy metals as main components [4], [5]. After evacuation to sludge fields, these turn into gel-like solids which occupy vast suburban fields. The utilization of sewage sludges is an actual problem for all world community. Due to the presence of micro- and macroelements, vitamins, aminoacids, beneficial microorganisms and organic matter, the most rational approach to the utilization of the sewage sludges is their usage as an agricultural fertilizer after partial removal of heavy metals (HMs) [2], [3]. As to the chemical composition, sewage sludges occupy intermediate position between microbial biomass and soil [6]. So, for HMs removal from sludges it can be used the approaches proposed for remediation of soils contaminated by heavy metals [7], [8]. These approaches stipulate the initiation of biological process supplying the sludge system with metabolites (e.g. oxycarboxylic, carbonic acids, hydroxyls, etc.) capable to form stable, ecologically friendly water soluble or ultracolloidal complexes with heavy metals [7], [8].

Authors are with F. D. Ovcharenko Institute of Biocolloidal Chemistry NAS of Ukraine, 42 Acad. Vernadskoho Blvd., 03142, Kyiv, Ukraine (email: KirKa @bigmir.net).

There are some works on heavy metals bioleaching from sewage sludges in modern literature. It is proposed the process of HMs removal from active sludge by promotion of sulphur-oxidizing sludge biocenoses adding sulphur as an energy source [9]. Its duration achieves 30 days. The possibility of obtaining a fertilizer similar to commercial one by composting of HMs contaminated sewage sludge at temperature 60°C with food waste during two weeks is shown [10].

The aim of our investigation is to work out the process of heavy metals bioleaching from stabilized sewage sludge at middle temperatures with their utilization as a biomineral fertilizer.

II. MATERIALS AND METHODS

The object of this study was sludge wastes as a suspension stabilized (secured from pathogens) in anaerobic-aerobic conditions and as a gel-like solid.

For heavy metals removal from stabilized sludge the method of bioleaching (bioextraction) was used. This method is based on activation of autochthonous microbiota by adding necessary nutrients. For targeted regulation of metabolism of sludge heterotrophic biota 8g/L of sodium acetate (alcaligeneous vector) or glucose (acidogeneous vector) were added as a source of carbon and energy. For the promotion of sulphur-oxidizing activity (chemoautotrophic metabolism) in the stabilized sludge suspension 5g/L elemental sulphur was added. For metals bioleaching, sludge suspension was incubated at stirring, S:L (solid:liquid) ratio 1:10 and temperature 20-22°C until a constant pH value. Sludge samples without nutrients added (in distilled water at pH 6.8-7.0, weakly acidic or alkaline medium at pH 2.0-2.5 or 9.6-9.8, respectively) served as the controls of HMs chemical leaching. These controls were stirred for 2 hours up to establish equilibrium in test systems. Solid phase was separated by centrifugation and concentrations of desorbed metals were analyzed in supernatants by the atomic-absorption and X-ray-fluorescent methods. The methods are detailed described in [6].

The swelling of gel-like solid samples was assessed by gravimetric method. The content of organic matter was determined by the weight loss after ignition of the samples above 500°C during 1 hour.

Enterobacteria content as a direct indicator of pathogen levels was calculated by seeding on agarized ENDO medium.

The efficiency of the biomineral fertilizer was demonstrated in vegetation experiments. Aromatic herbs were used to study the influence of the fertilizer on plant growth in the pots. Fresh sandy soil with added fertilizer at an application rate of 4 % (weight of dry matter / weight of soil) placed in every pot. No fertilizer was added to the control. Its effect on the growth and yield of the plants over a period of 5 weeks was analyzed by weighting raw herbs after the release from soil and washing.

III. RESULTS AND DISCUSSION

The results of HMs removal from sewage sludge suspension under chemical leaching and bioleaching by metabolizing chemoautotrophic (sulphur-oxidizing) cenoses and heterotrophic ones were compared (Table I). At the example of zinc and chromium removal the longest leaching time in the chemoautotrophic microbial process (18–20 days) was found. The most rate of HMs solubilization and removal occurred in chemical (acidic) leaching.

The efficacy of HMs biological leaching (acidogeneous and alcaligeneous) from sludge suspension was closed to the effect of chemical extraction by acidic sollution. Chemical leaching in alkaline medium was non effective. The HMs solubilization activity varied from 83 % (Zn) up to 14 % (Cr) and corresponded to the following series: Zn (83-78%) > Mn (72-50%) > Cu (70-48%) > Ni (55-39%) > Co (52-32%) > Pb (27-19%) > Cr (18-14%).

It should be noted that after gel-like sludge solid swelling during 3 days it behaved similar to sludge suspension in the processes of HMs leaching [11].

The leaching of heavy metals was accompanied by sludge suspension destabilization. The most rapid sludge flocks sedimentation was observed in biological leaching processes, especially at alkaligeneous metabolize vector.

In HMs leaching processes the ratio of organic and mineral components in sludge sediments was altered. In biological extraction processes with the participation of heterotrophic biota considerable increase (up to 60 %) of organic component was occurred in comparison with the samples of chemoautotrophic biota activity (32 %), chemical (acidic) leaching (45 %) and control native sludge (52 %).

At similar efficiency, the processes of HMs removal with

heterotrophic biota have considerable advantages versus the processes with chemoautotrophic biota due to their hight speed and exclusion of secondary chemical pollution.

The results of the investigation of conditions for HMs leaching from sewage sludge after biological treatment of municipal waste water have served as a base of appropriate process of bioconversion of sewage sludge into fertilizer. Its scheme is shown in Fig. 1. This process includes the enhancing of vital ability of heterotrophic sludge biota by adding the easily metabolized nutrients, synthesis of metabolites by growing sludge cenoses. These metabolites with the properties of heavy metals extractants and sludge flocks flocculants provide sludge suspension sedimentation and flocks concentration. The sludge sediment is the biomineral fertilizer of prolonged action with immobilized bioelements.

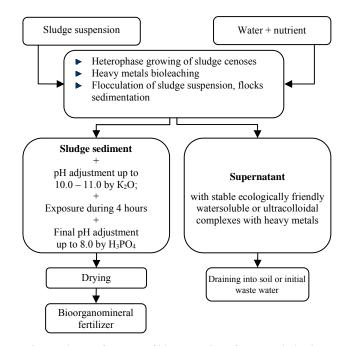


Fig. 1 Scheme of process of bioconversion of sewage sludge into fertilizer

 $TABLE\ I$ Parameters of Chemical and Biological Leaching of Heavy Metals From Sewage Sludge

			CHEMICAL PI	ROCESSES		
Example	DURATION, hours		pH_{t}	SEDIMENTATION RATE, mL·h ⁻¹ —	DESORPTION ACTIVITY, %	
ELUENT					Zn	Cr
Distilled water	2		6.8 - 7.0	0.4	10.0	1.3
HCl	2		2.0 - 2.5	1.2	83.0	18.0
NaOH	2		9.6 - 9.8	1.0	0.0	0.0
			BIOLOGICAL I	PROCESSES		
METABOLIZING CENOSES	NUTRIENT	DURATION, days	pH_t	SEDIMENTATION RATE, mL·h ⁻¹	DESORPTION ACTIVITY, %	
					Zn	Cr
Chemoautotrophic	Sulphur	20	2.5 - 3.0	10.0	81.0	15.0
Heterotrophic:						
acidogeneous	Glucose	2	3.5 - 4.0	19.0	80.0	15.0
alcaligeneous	Sodium acetate	2	9.2 - 9.4	22.0	78.0	13.5

As an alternative carbon sources it can be also used easily metabolized carbon sources (herbs, food wastes, etc.): protein or carbohydrate containing substrates for providing alkaligenous or acidogenous sludge metabolism, respectively.

The obtained sludge sediments with 99% humidity were additionally stabilized (secured from pathogens) in such a way: pH adjustment to 10.0-11.0 by dry K_2O , exposure during 4 hours, neutralization to pH = 8.0 by phosphoric acid and drying up to humidity value 40-60 %. As it is known [12], fertilizers with alkaline pH favorable for the formation of waterstable aggregates which are soil fertility indicator.

The composition of the fertilizer obtained is shown in Table II. In general, it satisfies the EU limits for the sewage sludge of agricultural utilization.

TABLE II
SOME CHARACTERISTICS OF THE FERTILIZER ON THE BASE OF SLUDGE
SEDIMENTS

PARAMETERS	FERTILIZER	EU LIMITS
Cu (μg · g ⁻¹)	136 – 150	1000
$Zn (\mu g \cdot g^{-1})$	190 - 220	2500
Mn ($\mu g \cdot g^{-1}$)	195 - 220	2000
Co (μg · g ⁻¹)	24 - 30	100
Pb $(\mu g \cdot g^{-1})$	53 - 60	750
Ni (μg·g ⁻¹)	50 - 60	300
$\operatorname{Cr}(\mu g \cdot g^{-1})$	550 - 600	1000
Enterobacteria (P.F.U. · g ⁻¹)	88 - 90	<100

Under the influence of organic acids excreted by growing plants, the sludge bioelements can be gradually released from immobilized state into environment absorbed by plants [13].

The fertilizers obtained were assayed in vegetation experiments. The results of plant growth are shown in Fig. 2. Use of the fertilizer provides a faster growth of herbs and increase harvest of 5–10 times as compared with control (unfertilized) soil.

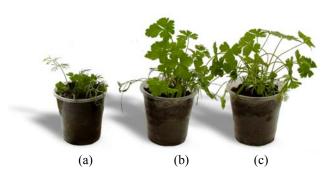


Fig. 2 Effect of fertilizer added to sandy soil on aromatic herbs growth (a) control, unfertilized soil; (b), (c) soil samples with sludge fertilizers obtained after heavy metals removal at bioleaching by heterotrophic cenoses with acidogeneous and alkaligenous metabolism vectors, respectively

IV. CONCLUSION

A new process for bioconversion of sewage sludge into fertilizer at middle temperatures was developed. It is based on promotion of vital ability of heterotrophic sludge biota by adding easily metabolized nutrients and complementary stabilization (rendering harmless) of sludge sediment in alkaline medium followed by partial neutralization and drying. The fertilizer satisfies the EU limits for the sewage sludge of agricultural utilization. Its application to the soil resulted in faster growth of agricultural plants.

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