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Analysis of the sorption complex in sandy soils fertilized with differently dried sewage sludge

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ABSTRACT

Sewage sludge is an important problem in sludge management. One of the options in sewage sludge management is using them as fertilizers provided that the provisions stipulated by the Ordinance of the Minister of the Environment are met. The aim of this study was to measure the changes in the properties of sorption complex in sandy soils fertilized with sewage sludge and manure. The sewage sludge after natural (drying beds) and solar drying was added to the sandy soil. Cattle manure was used for comparative purposes. The following doses of organic fertilizers were used: 0, 10, 20, 30 and 40 mg ha^{-1} calculated per experimental pot that contained up to 10 kg of sandy soil. Over the period of 12 months of the experiment, the changes in hydrolytic acidity and active acidity were analysed in the fertilized foundations. After analysing the obtained results, one can conclude that the use of sewage sludge and manure significantly impacted on the properties of sorption complex. The study confirmed that the use of sewage sludge had an essential effect on the phenomenon of acidification of soils which was observed during the determination of the hydrolytic acidity.

Keywords: Soil; Sewage sludge; Cattle manure; Sorption complex; Humic substances

1. Introduction

The problem of the use of sewage sludge is not new, but still it seems to be a topical issue. Ever-increasing number of wastewater treatment plants that treat sewage and sewage sludge makes it necessary to take up different actions aimed at management of this type of waste [1,2]. One of the methods of utilization of sewage sludge is their use in the environment for soil improvement. This method seems to be rational since fertilizing value of sludge has been confirmed. Sewage sludge is a reach source of nutrients for plants and stimulates soil-forming effect [3–5]. The fertilizing value of sewage sludge depends on the contents, such as nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca) and microelements. The sewage sludge provides soil with considerable amounts of organic matter and consequently improves its properties [6]. The content of organic matter is one

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of the major factors that determine fertilizing properties of sewage sludge. Its effectiveness is often compared to manure [7]. In raw sludge from biological sewage treatment, organic matter represents over 75% of dry mass. In fermented sludge, it accounts for ca. 50% of dry mass. Chemical reaction of most types of sludge is neutral or alkaline, which suggests a considerable content of calcium and magnesium compounds. The content of nitrogen and phosphorus in sewage sludge is often higher than in compost or manure. Sewage sludge might represent a valuable source of these biogenic substances for fertilized plants. Sewage sludge contains a number of valuable microelements (copper, nickel and zinc), necessary for proper growth of plants [8]. Among heavy metals are both fertilizing components (microelements) and those which cause substantial environmental nuisance (macroelements) [9]. According to the standards concerning the permissible use of sewage sludge in Poland, it is recommended that the contents of seven heavy metals and metalloids should be determined: copper, zinc, chromium, nickel, cadmium, lead and mercury [10]. Apart from the benefits that result from using these fertilizers, there is also a risk that toxic substances which they contain could get into the soil [11]. Properties of soil sorption complex are thought to be one of the most important elements which affect its fertility and properties of plants. Extended sorption complex is the element which immobilizes and absorbs a variety of soil contaminants. Characteristics of sorption complex are affected by e.g. organic matter, humic relationships which occur during decomposition of organic matter, clay materials, pH and hydrolytic acidity.

Therefore, the particular focus should be on the reaction and sorption properties of the soils which are fertilized with sewage sludge. This is important because of the frequent trace elements present in the sewage sludge, which, with low reaction of soils, might easily migrate to groundwater and vegetation [9].

2. Materials and methods

In order to demonstrate the effect of fertilizing with sewage sludge on sorption properties of sandy, degraded soils the authors carried out pot and field experimentation. The experiments were used to investigate the effect of using sewage sludge and manure on selected chemical parameters of the fertilized grounds. They were carried out for one year.

Selected physical and chemical properties of the research material used in the pot experiments are presented in Table 1.

The authors used in the experiments, for fertilizing purposes, the lightly sandy soil with granulometric composition of a loose loamy soil. The reaction of these soils (measured in H_2O) was 6.87. According to the guidelines of the Institute of Soil Science and Plant Cultivation used for determination of the degree of soil pollution with heavy metals, the contents of all the seven metals in the sandy soils used in the experiments were at the level of permissible values defined by the standards [12]. Concentration of heavy metals in the soils was below permissible level recommended for fertilization with sewage sludge [11]. Two types of sewage sludge that were sampled from Myszków wastewater treatment plant were used for fertilization under conditions of pot and field experiments. The sludge originated from different drying processes: natural drying in sludge drying bed plots located in the area of the plant and solar drying in a building. The sludge from this wastewater treatment plant is generated after biological processes of sewage sludge treatment in aerobic conditions (aeration tanks). For comparative purposes, fertilizing in all the experiments was also enhanced by using a natural fertilizer (straw-based cattle manure). Both sewage sludge and manure samples before the use for fertilization in all the fertilizing variants used in the experiments were stored for the period of six months. The contents of seven standard heavy metals (Cd, Cu, Ni, Pb, Zn, Hg and Cr) in the sewage sludge used for the experiments and in the manure did not exceed the permissible values that are prerequisites for their use in nature. The contents of heavy metals found in the sewage sludge allowed even for their agricultural use and soil reclamation for agricultural purposes [11]. The sanitary state of the sewage sludge determined before the experiments also allowed for its use in nature. No *Salmonella* bacteria were isolated and no helminths eggs (which are the main sanitary indicators that determine the possibility of using sewage sludge in nature) were found in the sludge. In the field experiment, the bed plots with the size of $10\,m^2$ were located in the soil with granulometric composition of a loose loamy soil with soil reaction of 6.87. The following doses of sewage sludge and manure were introduced (once) to the arable layer (with thickness of 20 cm): 10, 20, 40 and 50 mg dm ha^{-1}. Different combinations of research objects presented in Table 2 were used for the field and pot experiments (see Table 2).

The experiments were carried out with three repetitions. After obtaining the research mixtures in the experimental bed plots (field experiment) the authors sampled, from each experimental object, the soil at the amount of 3 kg from the layer of up to 20 cm (with three repetitions) to the polyethylene pots. The

Table 1
Physical and chemical properties of soil, sewage sludge and manure used in pot and field experiments

Parameter	Soil	Sewage sludge: Myszków (after natural drying)	Sewage sludge: Myszków (after solar drying)	Manure
Grain size	pgl	–	–	–
Organic substance, % dm	0.29	42.2	39.0	61.0
Reaction (pH_{KCl})	6.65	6.95	7.03	8.25
Reaction (pH_{H_2O})	6.87	7.01	7.2	8.01
H_h, mmol (+) kg^{-1}	62.4	170.3	–	–
S, mmol (+) kg^{-1}	20.4	890.4	–	–
Organic carbon, g kg^{-1} dm	13.40	218.4	215.0	246.6
Total nitrogen, g kg^{-1} dm	0.64	39.1	35.0	39.8
Available P, mg kg^{-1} dm	34.0	616.70	601.0	470.0
Available K, mg kg^{-1} dm	21.8	238.6	219.6	2260.0
Available Mg, mg kg^{-1} dm	55.6	893.6	901.0	994.3
Cr, mg kg^{-1} dm	10.4	17	19	2.1
Zn, mg kg^{-1} dm	75.0	908	913	132
Pb, mg kg^{-1} dm	17.8	21	23	7.3
Cu, mg kg^{-1} dm	12.6	139	142	21
Cd, mg kg^{-1} dm	0.4	2.1	2.3	1.2
Ni, mg kg^{-1} dm	10.3	102.5	120.0	2.2
Hg, mg kg^{-1} dm	0.003	1.6	1.82	0.11

Table 2
Fertilizers combinations and determination of individual soil mixtures in pot and field experiments

Object no. and symbol of combination	Combination	Fertilizer dose (kg bed^{-1})	Fertilizer dose (Mg ha^{-1})
1 Control (*P*)	Control (loosely loamy sand)—*P*	0	0
2 PMn10	Soil and sludge mixtures using sewage sludge	4.34	10
3 PMn20	from Myszków Wastewater Treatment	8.68	20
4 PMn30	Plant after natural drying—PM_n	13.02	30
5 PMn40		17.36	40
6 PMs10	Soil and sludge mixtures using sewage sludge	4.34	10
7 PMs20	from Myszków Wastewater Treatment	8.68	20
8 PMs30	Plant after solar drying—PM_S	13.02	30
9 PMs40		17.36	40
10 PO10	Soil mixtures with cattle manure—PO	4.34	10
11 PO20		8.68	20
12 PO30		13.02	30
13 PO40		17.36	40

experiment design also included a control object (without fertilization). The pot experiment was carried out in laboratory conditions. Next, in all soil mixtures with sewage sludge and manure (fertilizers' combinations in the Table 2), both under pot and field experiments, the authors sowed *Dactylis glomerata* grass. The humidity in all the experimental pots was maintained constantly through the whole vegetation season at the level of 60% of maximum water capacity. During vegetation in the beds, the authors watered the grasses sporadically in the periods of summer and high temperature (in order for the water amount to be similar in both variants of the experiment). Pot investigations were carried out to determine the comparability of the results of field experiments (under natural conditions) with the results obtained in laboratory conditions. In the fertilized soils (in pot and field experiments) after the vegetation period (nine months), the same chemical parameters and sorption complex properties were analysed. Throughout the experiments (in the third, sixth and nineth month), the authors also analysed the changes in the content of humic acids in fertilized soils.

Physical and chemical properties of the sewage sludge, cattle manure and fertilized soils were determined according to the methods generally accepted in soil science and agricultural chemistry [13]:

(1) Soil pH in the solution of 1 mol KCl and H_2O (potentiometric determination).
(2) Hydrolytic acidity and cation-exchange capacity (CEC) using Kappen methodology.
(3) Content of humic acids in soils, determined by means of extraction and precipitation with HCl.
(4) Organic carbon (Tiurin's method).
(5) Organic matter, determined by means of heating in a muffle furnace at the temperature of 550˚C.
(6) Total nitrogen, using a Kjeldahl distillation method.
(7) Available phosphorus and potassium: Egner-Riehm method.
(8) Content of heavy metals (zinc, lead, copper, cadmium, nickel, chromium and mercury) in the sewage sludge, manure and soils was determined after previous mineralization of samples in a microwave reactor (in the mixture of strong acids) using the method of atomic absorption spectrometry.

The experiments were carried out with three replications. The results are represented by means of these replications. The study of the results was carried out using a statistical software package STATISTICA 9.0. Comparisons of the variables analysed in the study used a two-way analysis of variance/covariance.

3. Results

The results of determinations of the sorption complex in the fertilized sandy soil under conditions of pot and field experiments are presented in Tables 3 and 4.

In the non-fertilized sandy soil after nine months of the experiments, soil reaction measured in water amounted to 6.84 (pot experiment) and 6.80 (field experiment). In all the objects fertilized with sewage sludge, the authors observed a decline in pH with respect to the control object. It was higher for the

Table 3
Properties of sorption complex in the fertilized sandy soil (pot experiment)

Object no.	Fertilizer combination	Contents									
		pH_{H_2O}		pH_{KCl}		Organic substance (%)		Hydrolytic acidity H_h (mmol (+) kg $^{-1}$)		Cation-exchange capacity CEC (mmol (+) kg $^{-1}$)	
		Mean	S.s.	Mean	S.s.	Mean	S.s.	Mean	S.s.	Mean	S.s.
1	Control (*P*)	6.84		6.62		0.30		67.33		20.13	
2	PMn10	6.68	**	6.40	**	0.45	**	85.33	**	36.00	**
3	PMn20	6.60	**	6.24	**	1.20	**	94.20	**	80.10	**
4	PMn30	5.90	**	5.44	**	1.85	**	105.10	**	154.00	**
5	PMn40	5.70	**	5.11	**	2.10	**	107.10	**	167.50	**
6	PMs10	6.88	n.s.	6.64	n.s.	0.67	**	107.10	**	40.00	**
7	PMs20	6.79	*	6.46	**	1.68	**	124.00	**	114.10	**
8	PMs30	6.70	**	6.38	**	2.60	**	135.67	**	234.20	**
9	PMs40	6.24	**	6.10	**	3.97	**	150.10	**	247.00	**
10	PO10	6.97	**	6.69	*	0.69	**	124.00	**	147.20	**
11	PO20	7.18	**	7.10	**	1.43	**	120.60	**	194.00	**
12	PO30	7.24	**	7.16	**	2.11	**	114.60	**	264.20	**
13	PO40	7.50	**	7.40	**	2.93	**	84.10	**	354.46	**

Note: Significance of differences compared to the control object.
*$p < 0.05$.
**$p < 0.01$.
n.s.—the difference not statistically significant.
S.s.—statistical significance.

Table 4
Properties of sorption complex in the fertilized sandy soil (field experiment)

		Contents									
		pH_{H_2O}		pH_{KCl}		Organic substance (%)		Hydrolytic acidity H_h (mmol (+) kg $^{-1}$)		Cation-exchange capacity CEC (mmol (+) kg $^{-1}$)	
Object no.	Fertilizer combination	Mean	S.s.	Mean	S.s.	Mean	S.s.	Mean	S.s.	Mean	S.s.
1	Control (*P*)	6.80		6.59		0.23		187.00		119.70	
2	PMn10	6.60	**	6.30	**	0.43	**	225.20	**	119.70	n.s.
3	PMn20	6.42	**	6.21	**	0.97	**	227.37	**	114.30	**
4	PMn30	5.54	**	5.39	**	1.25	**	247.60	**	114.50	**
5	PMn40	5.10	**	4.79	**	1.95	**	262.33	**	124.60	**
6	PMs10	6.79	n.s.	6.58	n.s.	0.62	**	259.20	**	110.00	**
7	PMs20	6.66	**	6.35	**	1.25	**	229.00	**	115.70	**
8	PMs30	6.50	**	6.21	**	2.33	**	217.20	**	120.47	n.s.
9	PMs40	6.20	**	5.59	**	3.45	**	202.33	**	129.70	**
10	PO10	6.78	n.s.	6.61	n.s.	0.65	**	189.10	n.s	142.70	**
11	PO20	7.14	**	7.00	**	1.97	**	177.65	**	143.30	**
12	PO30	7.18	**	7.13	**	2.57	**	170.00	**	145.40	**
13	PO40	7.40	**	7.37	**	3.90	**	165.60	**	154.45	**

Note: Significance of differences compared to the control object:
*$p < 0.05$.
**$p < 0.01$.
n.s.—the difference not statistically significant.
S.s.—statistical significance.

higher doses of the waste used. Fertilization with the manure had the opposite effect: it alkalized the soil environment. The obtained values of hydrolytic acidity were also increasing after application of sewage sludge and decreasing after fertilization with cattle manure. The obtained values of the reaction in all the pot research objects were higher than those determined under field experiment conditions. The content of organic matter in the control soil amounted on average to 0.30% (in pot objects) and 0.23% (in pot experiments). Fertilization with both sewage sludge and manure considerably increased the content of organic matter in the soils. The highest increase in the content of organic matter was found in the soils fertilized with the sludge after solar drying, both in pot and field experiments. Also in this case in the objects of field experiments, these contents were lower than in pot experiments. CEC increased with the dose of the fertilizer used. Besides, fertilization with the sludge after solar drying caused the highest increase in this parameter.

The results of changes in the content of humic acids in the fertilized sandy soil under conditions of pot experiment are presented in Figs. 1–3, and, the results for the field experiments are illustrated in Figs. 4–6. Data analysis contained in Figs. 1–6 showed that fertilization with sewage sludge caused a higher increase in the amount of humic acids in soils compared to the soils fertilized with natural organic fertilizer i.e. cattle manure. It was found that sewage sludge after solar drying introduced to soil for

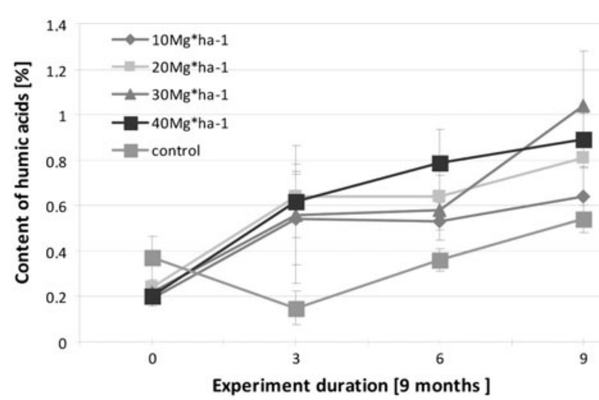

Fig. 1. Content of humic acids in sandy soil fertilized with sewage sludge after natural drying (pot experiment).

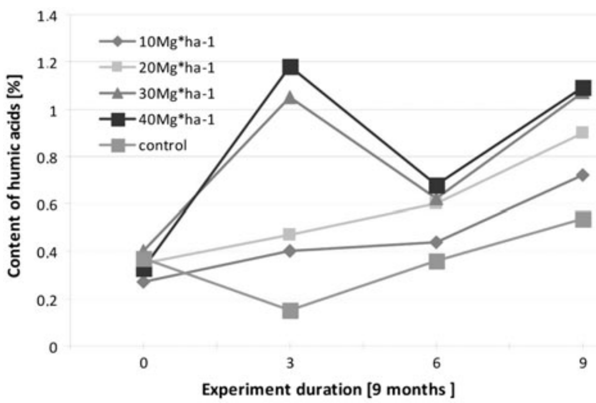

Fig. 2. Content of humic acids in sandy soil fertilized with sewage sludge after solar drying (pot experiment).

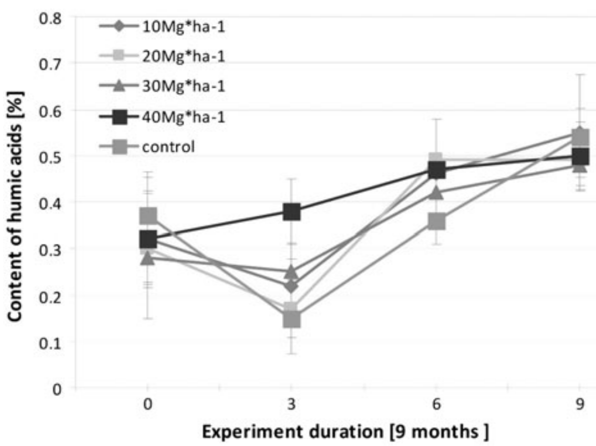

Fig. 3. Changes in the content of humic acids in sandy soil fertilized with manure (pot experiment).

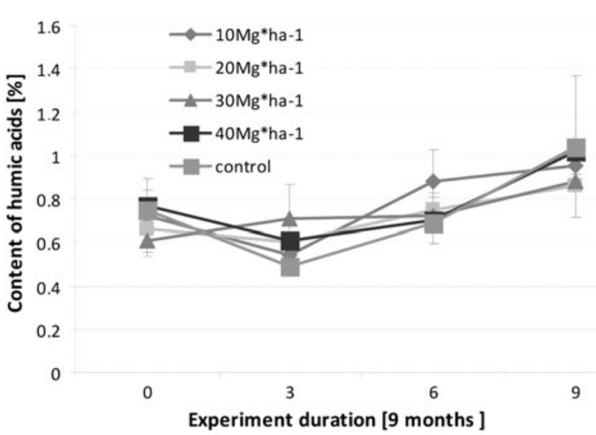

Fig. 4. Changes in the content of humic acids in soil fertilized with sewage sludge after natural drying (field experiment).

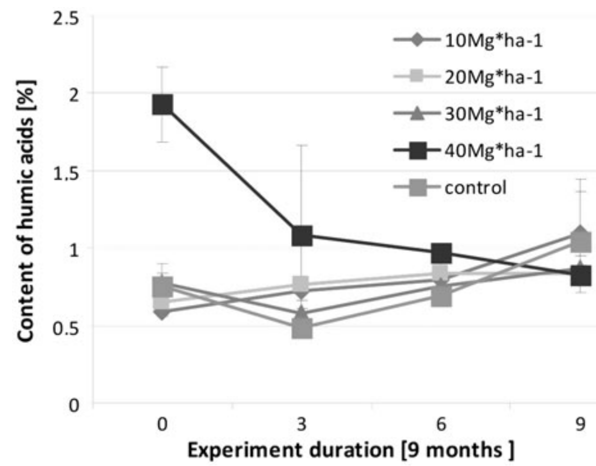

Fig. 5. Changes in the content of humic acids in soil fertilized with sewage sludge after solar drying (field experiment).

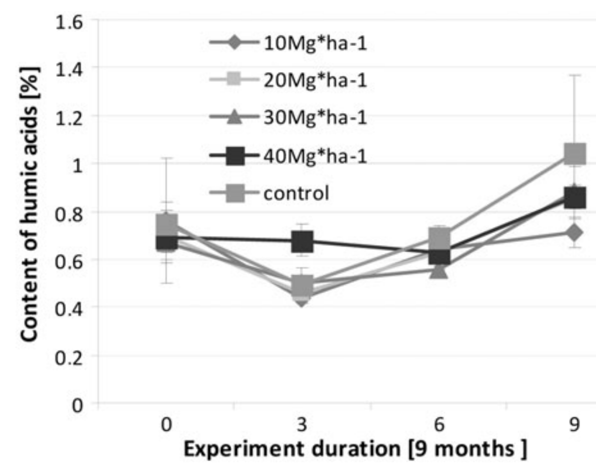

Fig. 6. Changes in the content of humic acids in soil fertilized with manure (field experiment).

fertilizing purposes caused an increase in the content of humic compounds in soil which was higher than in the sludge dewatered with belt presses.

4. Discussion

The sludge and manure used in the study significantly contributed to changes in the properties of sorption complex and contents of humic acids, both under conditions of pot and field experiments.

A decline in the value of pH and an increase in potential acidity (H_h) in the soil after application of sewage sludge, similar to the present study, has also been observed by other authors [14,15]. Similar effect of sewage sludge on the levels of soil acidity was demonstrated by Iżewska [16], who investigated the effect of fertilization with manure and sewage sludge on soil properties and by Stańczyk-Mazanek et al. in previous experiments [8]. Gondek [17], who analysed fertilization use of sewage sludge, also demonstrated their acidifying properties, particularly in the second year after fertilization. Unlike sewage sludge, manure caused a decline in soil acidity in all the research objects, which was higher with the fertilizing dose. Different results were obtained by Skowrońska and Filipek [18], who found an increase in soil acidity after application of both sewage sludge and manure.

Other authors have found an increase in pH after introduction of sewage sludge to soils. However, this might result from the properties of individual types of sewage sludge (e.g. liming before storage). The effect of instability of pH after fertilization of soil with sewage sludge was also observed in the study by Greinert et al. [19]. Furthermore, Walter et al. [20] did not show the effect of utilization of the sewage sludge on soil reaction.

Lower active acidification of soil was caused by the sludge after solar drying, both under conditions of pot and field experiments. However, potential acidity (H_h) indicated a more noticeable tendency for a long-term acidification of the environment in the case of sewage sludge after solar drying. An increase in hydrolytic acidity by 50% in the soils after fertilization with sewage sludge compared to control samples was determined in the study by Skowrońska and Filipek [18]. Other observations were obtained by Baran et al. [21], since they found a decline in hydrolytic acidity after fertilization with composts from sewage sludge compared to control objects. However, this different reaction could be explained by the method of sludge compost preparation, since a considerable amount of ashes with alkalizing properties were added. Fertilizing with both sewage sludge and manure caused the CEC in the fertilized soils to increase. This phenomenon was the most noticeable after solar drying of sewage sludge. During the pot and field experiments, the use of all the organic waste and manure caused an increase in the content of humic compounds in the soils. The obtained results included in Figs. 1–6 show that fertilization with sewage sludge caused a higher increase in the amount of humic acids in soils compared to the soils fertilized with natural organic fertilizer i.e. cattle manure. Similar results were demonstrated by [22,23]. After one vegetation season, the highest content of humic acids was observed in sandy soil fertilized with the sewage sludge after solar drying, both in pot and field experiments. Comparison of the results obtained in both pot and field experiments showed a faster decomposition of humic compounds in the soils dried in natural conditions. Under field conditions, the organic substance in the fertilized soils decomposed faster with respect to the research objects (pots) maintained in laboratory conditions. The soil reaction was also significantly higher in field experiments compared to pot experiments.

5. Conclusions

When analysing the obtained results, it was found that the use of sewage sludge and manure significantly impacted on the properties of sorption complex. The study confirmed that the use of sewage sludge had an essential impact on the phenomenon of acidification of soils which was observed while determining the hydrolytic acidity. Only manure used for fertilization caused a rise in acidity, both active and potential one. CEC rose with an increase in fertilizers doses of sludge during pot and bed experiments. Sewage sludge after solar drying contributed to a larger extent to the improvement in sorption properties of the fertilized soils compared to the sludge after natural drying. However, the organic conventional fertilizer (manure) turned out to be the best fertilizer to improve the characteristics of sorption complex.

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