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Research on Potential Application of a New Fertilizer based on Natural Sorbents for Toxic Soils

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The article considers the study on potential application of fertilizer containing natural sorbents from Kazakhstan deposits in order to develop a new organomineral fertilizer from household waste water and sorption materials. There was the study on the possibility for the developed organomineral fertilizers to influence heavy metals input into plant products, including those ones on polluted soil. There was the research on heavy metals input into soil with meltwater on urban territory plots close to metallurgic enterprises in order to apply the proposed new fertilizer. The following factors were defined: the required area of the plots, their service life period, produced fertilizers application load, economically reasonable distance for transporting fertilizers. The work demonstrates test results related to studying influence of new fertilizer types on Amoria creeping clover (Trifolium repens) feeding crop capacity, accumulation of heavy metals in soil and plants. Content of heavy metals was defined in plant products grown with new fertilizers application and it was proved that the proposed fertilizers were safe. Heavy metals content in plants decreases on 2.3 - 10.2 % of heavy metals content in soil if there is fertilizer based on shungite. Shungite-based fertilizer provides better results in copper and zinc than bentonite-clay based fertilizer (from 0.6 to 6 % of heavy metals content in soil). But bentonite-clay based fertilizer provides better results in cadmium and lead (0.4 - 1.9 %).

1. Introduction

One of environmental problems in big cities is utilization of domestic wastewater sludge. As a rule, after mechanical mud is dewatered under natural conditions, sludge is stored on the territory of waste treatment facilities at sludge draining beds or temporary storage areas and it is not further utilized. The issues of treatment and utilization of domestic wastewater sludge are relevant for all big water service companies and represent a serious problem. Basic existing methods of utilization are burning, dumping and using as a fertilizer. When research results conducted in our country and abroad were analyzed, it was found that most process flows for waste water treatment are based on the method of biological purification in aerotanks. However, this method doesn't provide the required efficiency of pollutant removal. As urban waste water sludge is mass with high content of organic compounds, the main direction for its utilization is its use as a fertilizer.

When urban wastewater which is the mixture of household waste water of residential districts, domestic and surface water flows from industrial enterprises is treated, utilization of formed sludge is a hardly-solved problem (Tan et al., 2021), because in this case sludge contains toxic components (Santos et al., 2021). The researchers engaged in the problem of domestic wastewater sludge utilization and development of unconventional fertilizer types on its base (Kominko et al., 2017), distinguish a range of problems such as high hazard class due to heavy metals content in concentrations exceeding MAC, and consequently, limited use of such fertilizers in agriculture (Delibacak et al., 2020).

Heavy metals behaviour in soil is defined by its composition and properties. Depending on certain conditions, heavy metals ions in soil solution can fix on the surface of different soil components and this will define their further behaviour in soil. Such microelements as boron, cobalt, copper, manganese, molybdenum, selenium, zinc are necessary for plants growth. However, if metals concentration in soil is high, they can be toxic for plants and thus decrease crop yield. Metals that are not necessary can be toxic for plants and decrease crop yield.

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Metals available for plants and amenable to leaching are present in soil solution in the form of free metal ions, complexes and chelate compounds. During absorption by plants or leaching, there is a balance between soil solution and solid phase. This causes relatively constant metals concentration of metals in soil solution. Metals solubility and their availability decrease as pH increases.
Metals in soil solution constantly interact with metals in soil in the form of sediments related to soil organic matter, absorbed by clay minerals and delayed by hydroxides. Metals in soil in the form of cations that are capable for exchange are immediately available for absorption with plants, However, numerous researches proved that only a few metals input into soil are capable for exchange (Li et al., 2019).
Some researchers (Geng et al., 2020) analyzed origin and chemical composition of heavy metals in sediments and consider eco-efficient extraction of heavy metals from wastewater sludge by passive sorption and active absorption of biomass. Potential materials that can serve as an additive for developing fertilizer from waste water sludge are natural sorbents such as zeolite (Kotoulas et al., 2019), montmorillonite bentonite clay, as well as compositions of sorbents with different additives. The conducted studies proved that zeolite and calurea additives to fertilizers contribute to improving plants growth and crop yield (Lestia et al., 2018). Other authors (Ovchinnikov et al., 2021) provided researches on wastewater sorption by means of combined charging of zeolite and activated carbon with their further use as fertilizers. Also, biochar and zeolite were added in fertilizers and thus plants growth was improved (Kocatürk-Schumacher et al., 2018). The use of chitosan- montmorillonite bubbles also provided fertilizers efficiency as they contain montmorillonite clay which has the best sorption properties (Santos et al., 2015).
Ust-Kamenogorsk waste treatment facilities sludge containing heavy metals was studied. They come together with waste to treatment facilities and then they are concentrated in sludge in the process of purification. Waste water that goes to biological purification in aerotanks contains Fe, Cu, Zn, Mo, Cd, Pb, Pd and other elements in concentrations from 0.0004 to 10.79 mg/dm^3. The concentration of zinc, copper and lead is the highest. Metals are in the form of ions in sediments this causes their mobility and easy distribution in the environment. It is hard to utilize such sludge, however taking into account properties of natural aluminosilicates, it is possible to use them as a fertilizer under conditions that mobility of heavy metals ions in sludge is decreased after their treatment with natural sorbents.

2. Materials and methods of research

To define the degree of soil contamination, samples of snow were taken and melt water from different areas of Ust-Kamenogorsk and beyond by wind rose was analyzed in order to identify qualitative and quantitative indicators of heavy metals input into soils with melt water. Snow samples were taken in the end of winter period (March-April) before the beginning of snow melting. Snow cover samples were taken to the laboratory; snow was melted at room temperature. Then content of different components in melted water was defined with inductively coupled mass spectrometer ICP-MS Agilent 7500cx (Agilent, 2019).
Element-by-element chemical composition and microstructure of dry and heat-treated dry extract of melted water were studied on scanning electron microscope JEOL JSM 6000.
To develop a new organomineral fertilizer, Koksu deposit shungites (Almaty region), and Tagan deposit bentonite clay of horizon 14 (East Kazakhstan) were studied as additives to domestic wastewater sludge.
Shungite is a cost-effective alternative for producing organomineral fertilizer due to its structure and obvious sorption properties. As a sorbent, shungite is characterized by a range of positive characteristics: high sorption and catalytic properties, chemical resistance, high mechanical strength, capability of absorbing different substances of organic and non-organic compounds. Shungite of Koksu deposit is represented by two modifications – schistous and carbonate. Koksu deposit raw materials refer to intermediate-carbon and shungite rocks by their carbon content. Carbonate shungite differs from schistous shungite by high carbon content (4.5 - 12 %). Average chemical composition of carbonate shungite is as follows (mass. %): SiO_2 –35.5; Al_2O_3 – 7; Fe_2O_3 - 4.52; CaO – 32.0; K_2O – 2.25 (Yerbolov and Daumova, 2022). The work (Aubakirova et al., 2020) identified the best sorption properties of shungites. Also Efremov et al. (2021) proved, that shungites modified with ferrous chloride (III) and manganese oxide (IV) are applied in the sphere of soil protection from contamination with different pollutants, for example, toxic components of propellant. Koksu shungite reserves enable to supply enterprises of Kazakhstan, near and far abroad with carbon raw materials of stable quality.
There is Primanrak group in Kazakhstan – Tagan, Manrak, Dinozavr deposits of bentonite clay. Bentonite clay of Tagan deposits differs from other clays by better sorption and physical and chemical properties, and also by montmorillonite minerals content which exceeds 90 %. Chemical composition of bentonite clays from horizon 14 is as follows (mass. %): SiO_2 – 55.48; TiO_2 – 0.30; Al_2O_3 – 19.38; Fe_2O_3 – 4.40; CaO – 1.98; MgO – 2.18; K_2O – 0.51; Na_2O – 0.14; SO_3 – 0.18 (Mamyachenkov et al., 2017). Natural sorbents are chosen as an additive to fertilizers considering properties related to heavy metals proved by the researchers of scientific and practical works.

To assess products quality that were grown in contaminated soil in the presence of fertilizers with the use of sorbents, the area located from downwind in relation to non-ferrous metallurgy enterprise was chosen. This site is 1 km from Ust-Kamenogorsk metallurgic complex of Kazzinc LLP.

A combined sample of soil was taken preliminarily on the site. Samples were taken in accordance with GOST 17.4.4.02-2017 «Nature protection. Soils. Methods for sampling and preparation of soil for chemical, bacteriological, helmintological analysis» (GOST, 2019). Soil samples for analysis were prepared in accordance with ST RK ISO 11464-2012 «Soil quality. Preliminary treatment of samples for physical and chemical analysis» (ST RK, 2012).

The plot was divided into three zones for obtaining comparative data about the quality of the grown products – zone 1 was sowed with plants without fertilizer addition, zone 2 – produced fertilizer with the use of shungite raw material was preliminarily input into soil; zone 3 - produced fertilizer with the use of Tagan bentonite was preliminarily input into soil.

Amoria creeping clover (Trifolium repens) feeding crop was chosen as test-plants in order to identify pollution of plant products with heavy metals and hazard of their further distribution in food chain. Before sowing, the plots were cleaned from stones, weed plants, and then they were levelled. As vegetation period began grass was seeded into wet soil of the prepared plots 0.5 cm deep, assuming that the seeding rate is 30 g of seeds/5 m^2. After that seeds sprouting test plants were watered and observed. In the end of vegetation period test-plants condition was assessed, then they were gathered, separated from roots, washed and dried.

3. Experimental part

The work covers the choice of the plot for applying the produced fertilizers, and dependence of soil loads on heavy metals content in the produced fertilizers. When sludge is used, the period of the plot exploitation depends on total amount of lead, copper, nickel, and cadmium input into soil. Their MAC are established so that to provide growth and use of crops at any time in future. Taking into account MAC values (Minister of Health of the Republic of Kazakhstan, 2021) and heavy metals content data in Ust-Kamenogorsk waste treatment facilities sludge, working loads of these metals sludge was calculated (Table 1).

Table 1: Working load of sludge on soil by heavy metals

Metal	Total MAC of metal, kg/ha	Metal content in sludge mg/kg	Working load of sludge, t/ha
Lead	1,120	260	4,300
Zinc	560	2,009	280
Copper	280	200	1,400
Nickel	112	240	470
Cadmium	11	24	460

It is commonly known that significant amount of heavy metals come into soil together with atmospheric precipitation, in particular, with melted water. Besides, during winter season pollutants are accumulated and concentrated in melted water and then they come into soil for a short time period. It should be considered when the produced fertilizers are used on these territories, because heavy metals coming into soil with atmospheric precipitation will influence the load and period which is allowed for fertilizers use on this plot.

As cost-effective distance for transporting of the produced fertilizers is 50 km, it should be considered that soils close to Ust-Kamenogorsk are under considerable technogenic influence for a long time. It should be noted that big non-ferrous-metallurgy enterprises are concentrated on the territory of Ust-Kamenogorsk. Soils of forests and agricultural fields that are close to mining and metallurgy enterprises activities, and populated areas are contaminated with heavy metals which continue coming into soils via atmosphere and hydrosphere.

The concentration of pollutants is up to 15 mg/dm^3 on the plots close to industrial enterprises and highways (Table 2).

Table 2: Elements content in melted water from different plots

Sample	Fe, mg/dm^3	Cu, mg/dm^3	Zn, mg/dm^3	Pb, mg/dm^3	Cd, mg/dm^3
1	18.99	2.894	79	1.80	2.08
2	24.17	2.459	239	1.98	1.32
3	6.36	4.395	489	1.39	10.32
4	6.01	14.261	11,780	60.49	502.10
5	4.24	24.140	15,000	349.60	561.00
6	37.71	8.889	1,342	83.76	48.57

Heavy metals in melted water are not only in solution, but also in solid particles composition. Electron microscopic study of dry and heat-treated solid extract of melted water (Figure 1) show that there are heavy metals (Zn, Pb, Cd, Cu). It should be noted that they come with atmospheric precipitation. So the use of the new fertilizer is relevant for decreasing toxicity, load on soil and for plot service life extension.

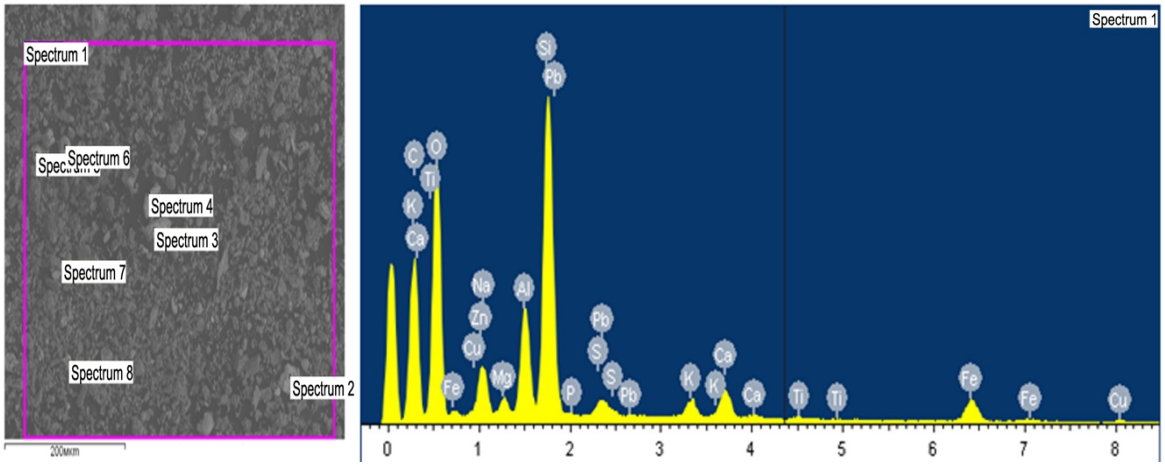
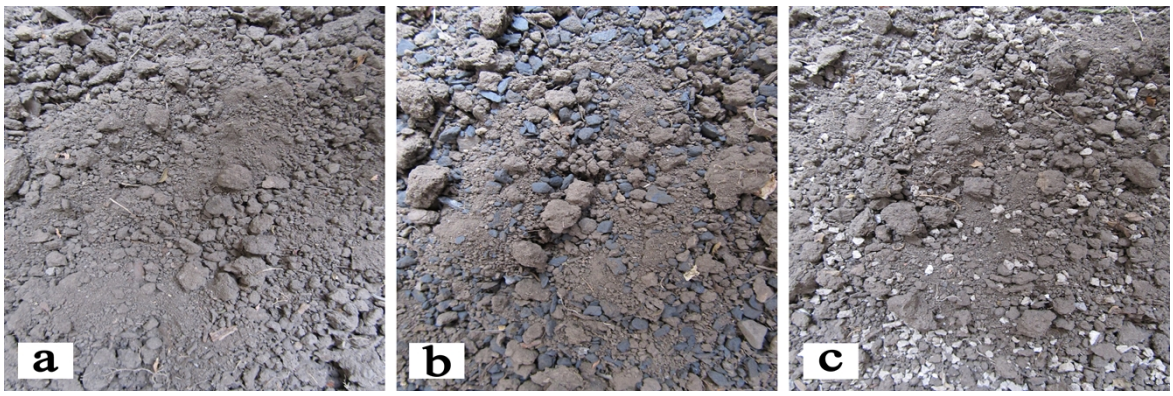


Figure 1: Element composition of melted water dry extract

The quality of products grown on contaminated soil were assessed in the presence of fertilizers with the use of natural sorbents. Figure 2 shows prepared soil of the test plot with and without fertilizers from shungite and bentonite clay.



a – soil without fertilizer, b – soil with fertilizer based on shungite, c – soil with fertilizer based on bentonite clay

Figure 2: Prepared soil of the test plot

The results of observations over sprouts of test-plants are provided in Table 3.

Table 3: Heavy metals content in soil and plants

Sample	Metal content			
	Cu	Zn	Cd	Pb
Without fertilizer				
Content in soil, mg/kg	12.32	41.82	0.82	21.15
MACs in soil, mg/kg (Minister of Health of the Republic of Kazakhstan, 2021)	33	55	0.5	32
MACs excess, times	0.37	0.76	1.63	0.66
Content in plants, mg/kg	2.25	3.26	0.10	1.53

Table 3 (continuation): Heavy metals content in soil and plants

Sample	Metal content			
	Cu	Zn	Cd	Pb
Without fertilizer				
MACp in plants, mg/kg (Chief State Sanitary Doctor of the USSR, 1986)	0.1	10	50	0.5
MACp excess, times	0.22	0.07	0.99	3.05
% of content in soil	18.22	7.79	12.12	7.21
With fertilizer based on bentonite clay				
Content in soil, mg/kg	13.81	43.40	0.90	23.82
MACs excess, times	0.42	0.79	1.80	0.74
Content in plants, mg/kg	1.93	2.44	0.07	0.84
MACp excess, times	0.19	0.05	0.71	1.67
% of content in soil	13.99	5.61	7.91	3.51
With fertilizer based on shungite				
Content in soil, mg/kg	20.42	51.34	1.00	29.22
MACs excess, times	0.62	0.93	2.00	0.91
Content in plants, mg/kg	1.63	2.60	0.10	1.14
MACp excess, times	0.16	0.05	0.98	2.28
% of content in soil	7.99	5.06	9.81	3.90

4. Results and discussion

The obtained data provided in Table 3 shows shungite efficiency that is contained in fertilizer made of domestic wastewater sludge. So heavy metals content in plants decreases on 2.3 - 10.2 % of heavy metals content in soil if there is fertilizer based on shungite. Shungite-based fertilizer provides better results in copper and zinc than bentonite-clay based fertilizer (from 0.6 to 6 % of heavy metals content in soil). But bentonite-clay based fertilizer provides better results in cadmium and lead (0.4 - 1.9 %).

The research showed that Koksu shungite can be used for expansion of resource base for producing organomineral fertilizers made of domestic waste water sludge. Lower concentrates of heavy metals in plants can be achieved even on contaminated soils (1.2 - 2.3 times less than heavy metals content in soils). The obtained results can serve as the basis for the following conclusion: it's possible to use contaminated soils for recultivation in case shungite-based and bentonite clay-based fertilizers are applied. Thus, natural sorbents adsorb and neutralize potentially hazardous chemical compounds.

5. Conclusions

The peculiarities of the produced fertilizers use on soils contaminated with heavy metals were considered.

The data obtained from electron microscopic study of dry and heat-treated solid extract of melted water enabled to identify such hazardous elements as copper, zinc, cadmium, lead and others. Besides pollutants concentration achieves up to 15 mg/dm^3 on the plot close to industrial enterprises and highways.

The work comprises the research on the possibility to use organomineral fertilizers based on waste water sludge and natural sorbents on the soils contaminated with toxic metals.

The produced organomineral fertilizer can be effectively used on contaminated soils for recultivation due to high sorption properties of Koksu shungite. It will enable to decrease heavy metals content in plant products 1.2 - 2.3 times of heavy metals content in soils. Also according to the obtained test results we can recommend Tagan deposit bentonite clay from horizon 14 as an additive to wastewater sludge.

Amoria creeping clover (Trifolium repens) feeding crop enabled to identify pollution of plant products with heavy metals and hazard of their further distribution in food chain.

The conclusions made and recommendations can be used at enterprises engaged in treatment of urban waste water. They also can be widely used in other spheres where there is a problem of fluid and solid media contamination with heavy metals. The developed method of sludge treatment will enable to solve the problem of their utilization thus providing environmental safety.

References

Agilent., 2019. ICP-MS Agilent 7500 cx inductively coupled plasma mass spectrometer manufactured by Agilent Technologies. <www.myco-analytical. com/product/agilent-7500cx-icpms>. accessed 13 March 2019.

Aubakirova R., Daumova G., Seraya N., Afanasenkova I., 2020. Sorption extraction of heavy metal Ions from wastewater by natural and synthetic sorbents. Chemical Engineering Transactions, 81, 343-348.

Chief State Sanitary Doctor of the USSR (4089-86), 1986. MPC of heavy metals in food raw materials and food products, <files.stroyinf.ru/Index2/1/4293731/4293731790.htm>, accessed 31 March 1986 (in Russian).

Delibacak S., Voronina L., Morachevskaya E., Onguna A.R., 2020. Use of sewage sludge in agricultural soils. Eurasian Journal of Soil Science, 9 (2), 126-139.

Efremov S., Nechipurenko S., Tokmurzin D., Kalugin S., Tassibekov K., 2021. Remediation of soil contaminated by toxic rocket fuel components using modified carbon-mineral adsorbing material produced from shungite rock modified with Mn^{4+} and Fe^{3+}. Environmental Technology and Innovation, 24, 101962.

Geng H., Xu Y., Zheng L., Gong H., Dai L., Dai X., 2020. An overview of removing heavy metals from sewage sludge. Achievements and perspectives. Environmental Pollution, 266 (2),115375.

GOST, 2019. 17.4.4.02-2017 Nature protection. Soils. Methods for sampling and preparation of soil for chemical, bacteriological, helmintological analysis, <docs.cntd.ru/document/1200158951>, accessed 01 January 2019 (in Russian).

Kocatürk-Schumacher N. P., Zwart K., Bruun S., Jensen L. S., Sørensen H., Brussaard L., 2018. Recovery of nutrients from the liquid fraction of digestate: Use of enriched zeolite and biochar as nitrogen fertilizers. Journal of Plant Nutrition and Soil Science, 000, 1-9. DOI:10.1002/jpln.201800271

Kominko H, Gorazda K., Wzorek Z., 2017. The Possibility of organo-mineral fertilizer production from sewage sludge. Waste and Biomass Valorization, 8(5), 1781–1791.

Kotoulas A., Agathou D., Triantaphyllidou I., Tatoulis T.L., Akratos C.S., Tekerlekopoulou A.G., Vayenas D. V., 2019. Second cheese whey treatment using zeolite under continuous flow mode and its application on wheat growth. Water, 11, 928.

Lestia D., Taofik A., Aliah H., 2018. Effect of zeolite size measures and urea fertilizers to growth and yield endive plant (Cichorium endivia L.). IOP Conference Series: Materials Science and Engineering, 434, 012121.

Li C., Zhou K., Qin W., Tian C., Qi M., Yan X., Han, W., 2019. A Review on heavy metals contamination in soil: effects, sources, and remediation techniques. Soil and Sediment Contamination: An International Journal, 28(4). 380-394.

Mamyachenkov S.V., Adryshev A.K., Seraya N.V., Khairullina A.A., Daumova G.K., 2017. Nanostructured complex sorbent for cleaning heavy metal Ions from industrial effluent. Metallurgist, 61, 615–623.

Minister of Health of the Republic of Kazakhstan (Order No. KR DSM-32), 2021. On the approval of Hygienic standards for the safety of the habitat, <adilet.zan.kz/rus/docs/V2100022595>, accessed 21 April 2021 (in Russian).

Ovchinnikov A.S., Denisova M.A., Bocharnikova O.V., Bocharnikov V.S., Kuznetsova N.V., Kuznetsov Yu.V., Repenko T.V., Meshcheryakov M.P., 2021. Wastewater treatment from agricultural enterprises using sprinkler irrigation and utilizing sludge as a fertilizer. IOP Conference Series: Earth and Environmental Science, 659, 012058.

Santos B.R. dos, Bacalhau F.B., Pereira T. dos S., Souza C. F., Faez, R., 2015. Chitosan-montmorillonite microspheres: A sustainable fertilizer delivery system. Carbohydrate Polymers, 127, 340–346.

Santos J.D., Pontes M.D., Nobrega M.AD., Santiago E.F., 2021. Effects of substrates containing different concentrations of sewage sludge on physiological parameters and quality of Alibertia edulis (Rubiaceae) seedlings, Environmental Science and Pollution Research, 28 (20), 25984-25992.

ST RK, 2012, ISO 11464-2012 Soil quality. Preliminary treatment of samples for physical and chemical analysis, <online.zakon.kz/Document/?doc_id=32284277>, accessed 15 August 2012 (in Russian).

Tan L-V, Tran T., 2021. Heavy metal accumulation in soil and water in pilot scale rice field treated with sewage sludge. ChemEngineering, 5(4), 77.

Yerbolov S., Daumova G., 2022. Waste water purification from metal Ions by ultra-dispersed natural sorbents. Journal of Ecological Engineering, 23(1), 43–50.