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RECYCLING OF WASTE SLUDGE FROM WWTP "GORIĆ" VALJEVO USING THE PROCESS OF STABILIZATION AND SOLIDIFICATION

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ABSTRACT

The efficiency of wastewater treatment is not only measured by the quality of treated wastewater, but also by the efficiency of treatment and permanent disposal of sludge that is separated. In addition to harmless, the sludge also contains hazardous substances that are released from wastewater during treatment.

This work aims to obtain a neutral and harmless product by treating waste sludge with a stabilization and solidification process using modified MID-MIX technology. Physico-chemical analysis has shown that the obtained solidification or neutral, completely inert material, which has a use-value, can be safely disposed of in a sanitary landfill following EU (European Union) regulations. In terms of chemical composition, it is a mixture of crystal-bound organo-calcium, hydrophobic salts with a low moisture content of 5.8%.

The results show that the method is the most environmentally friendly and most economical for the treatment of sludge, which can be applied to other types of waste with minor modifications.

Keywords*: waste sludge*, *stabilization, solidification, neutral*

INTRODUCTION

In wastewater treatment processes, sludge appears as a by-product, which is a waste of the technological process. Its processing and disposal is a special problem due to the content of heavy metals and other harmful substances, which, due to their character and chemical composition, cannot always be disposed of in municipal waste landfills [1,2]. The choice of the appropriate solution and location of disposal depends on the quality and quantity of the generated sludge, legal aspects, local conditions, and investment costs [3]. The treatment costs in some cases approach the costs of wastewater treatment [4]. Although the choice of the sludge treatment process and its final disposal is often far more complex than the wastewater treatment process, it is not given due attention [5].

Only thermally treated sludge, regardless of the stage (thermal conditioning, drying, pasteurization, and composting) is considered harmless and its use is allowed [6]. In some European countries, the practice is that sludge is applied directly as a fertilizer in agriculture after a certain treatment if it meets certain requirements regarding the content of heavy metals and other substances [7].

TEST METHODS

MID-MIX technologies

One of the technologies adapted for the treatment of waste generated after wastewater treatment (sewage sludge, bio-solids, leachate concentrates in landfills, etc.) is MID-MIX technology. At the heart of the technology is a process of solidification with stabilization.

Solidification is a term used for a wide range of treatments that change the Physico-chemical properties of waste in order to make it suitable for permanent disposal in a safe landfill,... [8]. The solidification process uses binders, additives, and impurities that help to sludge from a semi-solid and liquid state it turns into a solid form. The most commonly used stabilizing agents are cement, various types of pozzolana (fly ash, slag, cement kiln dust), and lime [9].

The input characteristics of waste are transformed into a completely new form of material. Each particle of waste material, with the help of water vapor molecules, encapsulates in a highly stable Ca lattice (membrane) and turns it into an inert stable powder, soldificate, or neutral. The speed of transformation (waste + additives → neutral) is very high and is less than 10-12 s. Once encapsulated, all affected particles become inert and have no mutual reactivity, which is the ultimate goal of processing [10]. Also, the pH value of waste increases, which improves the deposition of metals and their immobilization [11]. Sludge undergoing a solidification process must be stabilized and dehydrated.

The solidification/stabilization technique has shown significant potential in terms of solving the problem of contaminated tailings and large amounts of fly ash from thermal, power plants as well as red sludge from aluminum production [12]. It is also considered to be the best available technique for the treatment of solid and sludge waste at the UPOV (wastewater treatment plant) plant in Koprivnica [13]. It is also used for the treatment of liquid waste and sludge containing heavy metals and other hazardous contents [14].

The paper treats waste sludge using the process of solidification and stabilization. Besides, the effectiveness of the treatment was confirmed through the results of the Physico-chemical composition of the sludge and solidifiers.

Wastewater treatment plants WWTP "Gorić" Valjevo

Wastewater treatment plant "Gorić" in Valjevo performs combined treatment of domestic used water, infiltrated water, as well as a part of atmospheric water. They do not accept industrial waste belonging to the class of flammable (Group I), explosive, infectious, ionizing and radioactive materials. The recipient of the treated water is the river Kolubara, which is classified in the II category on the discharge profile.

Wastewater treatment includes stages of preliminary, primary and secondary treatment.

Figure 1. Shows the wastewater treatment plant in the city of Valjevo. The plant annually purifies about 6,525,488 m^3 of water and disposes of 2,225 tons of solid waste at the city landfill [15]. According to the rulebook on categories, testing, and classification of waste, Official Gazette, RS, 56/2010 and 93/2019. and based on previous tests, waste is classified as non-hazardous waste [16].

However, in its current state, it should not be disposed of in non-hazardous waste landfills. due to the high content of heavy metals, insoluble organic carbon, and increased moisture content. Waste sludge is brown-black in color, with an unpleasant odor. Physico-chemical treatment is recommended in order to reduce critical parameters.

Figure 1. Wastewater treatment plant in the city of Valjevo

The process of MID-MIX technology begins with the loading of sludge into the receiving basket, is crushed, and falls on the pre-reactor. Additives, in this case, quicklime, CaO, are added to the prereactor. Lime is added in a sufficient amount to raise the pH of 12, which creates an environment that is not suitable for the survival of microorganisms. As long as the pH is maintained at that level, the sludge will not rot, create unpleasant odors or pose a health hazard [17].

The oxidation-reduction reaction of vacuum-gas encapsulation is performed in the reactor. The retention time of the material in the reactor is 8-10 minutes. The finished product, neutral, comes out of the reactor. It is a powdery substance, grayish-white in color, with an increased amount of moisture that must be removed. The neutral goes further to the stabilizer, where it removes excess moisture with a slight vacuum and where the reaction practically ends. This product is ready for further use.

Sludge and soldificate samples were analyzed. Sampling and analysis were performed in an accredited laboratory. The National Law of the Republic of Serbia defines the Rulebook on categories, testing, and classification of waste [18]. It prescribes the use of USEPA Method 3051a [19], for testing the toxic characteristics of waste intended for disposal. The standard leaching test EN 12457-4 [20] is used for testing waste at hazardous waste landfills.

RESULTS AND DISCUSSION

The product of solidification is a light gray powder, weak in smell, does not absorb water, and has a completely harmless and neutral character.

The results of moisture, ash, and metal content in the samples are shown in Table 1. According to the Ordinance on waste categories and classification, Official Gazette of RS, 56/2010 and 93/2019 reference values refer to the limit values of components in waste for co-incineration [16].

Based on the attached test results, it is noticed that the concentration of heavy metals in the sampled sludge is below the limit value. This puts it in the group of non-hazardous waste. On the other hand, according to Directive 86/278/EEC, [21], in its current state, however, it cannot be disposed of in non-hazardous waste landfills. It contains heavy metals, insoluble organic carbon, and increased moisture content.

Table 1. Results of Physico-chemical analysis in samples of waste sludge and solidifies USEPA Method 3051a

Number	Perimeters	Waste sludge	Solid (neutral)	Limit
1.	Moisture content, %	79	5,8	/
2.	Ash content, %	58	1,8	/
	Metals, mg/kg			
1.	Arsenic	<0,9	<0,9	15
2.	Barium	29	14	200
3.	Cadmium	4,6	1,6	2
4.	Chrome	59	30	100
5.	Copper	48	42	100
6.	Mercury	0,19	<0,05	0,5
7.	Nickel	7,1	3,5	100
8.	Lead	12	8,7	200
9.	Antimony	1,3	4,4	5
10.	Zinc	206	128	400
11.	Vanadium	0,39	1,1	100
12.	Beryllium	<0,05	<0,05	5
13.	Tin	11	1,4	10
14.	Cobalt	1,1	0,94	20
15.	Thallium	<1,6	<1,6	3
16.	Calcium	/	24 %	/

After the process of solidification and stabilization, it was concluded that the metals were effectively immobilized in a mixture with lime. Chemical bonding of metals may involve the transformation of soluble forms of metals into insoluble silicates, hydroxides, or carbonates. Other changes can lead to the incorporation of metals by the mechanism of crystal adsorption [22].

The obtained neutral has a content of zinc 128 mg/kg, lead 8.7 mg/kg. The amount of cadmium in the sludge is 4.6 mg/kg, and after treatment, it is 1.6 mg/kg. This cadmium content is to be expected due to the fact that cadmium has the property of binding to non-volatile components of sludge. The average concentration of cadmium in raw sludge for Germany and selected European countries is 5 mg/kg of dry matter. The transfer coefficients for cadmium flows during incineration in a cement plant are 0.02 for waste gas and 0.98 for clinker [23]. Chromium is also largely found in the immobilized fraction. Thus, it does not pose a risk to the environment and is expected to be chemically stable and biologically inactive [24]. The ash content in the sludge is about 58%, and solidification has reduced it to 1.8%. The moisture content in the neutral is 5.8%.

The values of the analysis parameters from the EP extract (L/S=10/1) are shown in the Table 2. According to the Rulebook on waste categories and classification, Official Gazette of RS, 56/2010 and 93/2019, the reference values refer to hazardous waste landfills [16].

Dissolved organic carbon (DOC) was reduced from 1774 mg/kg to 406 mg/kg. The presence of DOC can increase metal leaching by several orders of magnitude. As a result, a new distribution will be established between DOC-bound metals and free metals.

Analyzes of EP extract tests indicate that the treated sludge is in terms of all indicators of satisfactory quality (according to the criteria of the Regulation on limit values) and that it can be used for useful purposes [25].

Conducted "in situ" experiments have shown that the application of the stabilization and solidification process is justified for the treatment of waste sludge. By retaining the effects of reduction, the expected products can be used without any interference ("Official Gazette of RS", No. 67/2011, 48/2012 and 1/2016) [25,26].

Table 2. Results of analysis in waste sludge and soldificate samples by standard leaching test EN 12457-4 [20]

Number	Perimeters	Waste sludge	Solid (neutral)	Limit
1.	PH value	7,6	12,8	6
2.	Electrical conductivity, µS/cm	1477	1070	/
3.	Solubility of solids (RDS), mg/dm^3	754	541	60000
4.	Fluorides, mg/kg	<1,0	<1,0	150
5.	Chlorides	45	603	15000
6.	Sulfates	3570	1026	20000
7.	Index fenola, mg/kg	<0,01	<0,01	1
8.	Soluble organic carbon, (DOC), mg/kg	1774	406	800
9.	Hexavalent chromium	<0,05	<0,05	/
10.	Ammonium ions	81	5,1	10000

According to the categorization of EU waste, the obtained solidification is a non-hazardous and completely inert material that has further use-value. It has a high content of calcium compounds (24%), low specific gravity: $0.910 > \rho > 0.915$ g/cm^3, floats on water, does not react, and does not mix with it. Analysis of dehydrated and dried samples of lime sludge formed by water softening in industry shows Ca contents, from 71.25% to 86.25% [27]. All this makes it good for use as an alternative raw material in production: cement, precast concrete elements, construction industry, civil engineering, and road industry [28].

Using the MID-MIX technology, the WWTP (Wastewater Treatment Plant) "Gorić" converts waste, ie sludge from wastewater into a form in which its constituents are immobilized so that they do not endanger the environment.

CONCLUSION

Sludge from wastewater treatment plants can be successfully converted into the form in which its constituents are immobilized using MID-MIX technology. The end product is neutral, a material with a new use-value - which can be used as a raw material or safely, in accordance with EU regulations, disposed of in a sanitary landfill. The test results show that there are no negative impacts from the aspect of environmental protection, safety, and human health.

MID-MIX technological process is one of the permitted and recommended technologies in Europe for industrial waste recycling - "BATNEC" - the best available technology that does not require excessive waste management costs and does not pollute the environment.

Based on the above, we conclude that the application of modern technologies in the segment of wastewater treatment significantly contributes to the preservation of the environment. Sludge as a by-product of wastewater treatment should be seen as a renewable source and not as waste. With the development of technology, new ways of recovery and final disposal of sludge are opening up. Fortunately, in the Republic of Serbia, the issue of sludge disposal has been resolved in a way that is enabled by MID-MIX technology, and recycling is an important form of environmental protection.

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