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TYPES AND VALORIZATION OF SLUDGE GENERATED IN WATER TREATMENT PROCESSES

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Abstract

This paper is a study on the problem of sludge formation in water treatment processes. Various physical and chemical processes used in technological systems of water treatment were described and those which are the source of sludge were indicated. The chemical composition of the sludge was presented, with particular emphasis on hazardous organic and inorganic pollutants. An essential part of the work was to consider the possibilities and ways of valorizing sludge. It was determined that the type of generated sludge depends on the applied process and its pollution degree depends on the type and quality of the water taken. Most of the sludge is formed during the coagulation process of surface waters, which may be contaminated with various heavy metals. Among the possibilities and methods of sludge valorization, an interesting way to use it is in construction, as an admixture to various building materials. It is also possible to use sludge as an unconventional adsorbent or reaction catalyst in the oxidation of organic pollutants present in wastewater.

Keywords: **Water treatment, Sludge.**

1. INTRODUCTION

Water treatment processes produce sludge that is a byproduct of the processes performed. The type of sludge formed depends on the process used for its treatment. In turn, the degree of sludge contamination depends on the type and quality of the treated water.

The most complex technological systems are used during the treatment of surface waters, which may be contaminated with various organic and inorganic compounds [1]. For this reason, the surface water treatment plant can generate the most sludge with different physical and chemical properties due to the location of the water intake.

The study researched the problem of sludge in water treatment processes in terms of sources of its formation, the degree of contamination and the possibility of its valorization.

2. WATER TREATMENT PROCESSES AND SLUDGE GENERATION SITES

The designation of water for drinking or technological use is conditioned by numerous legal regulations and sanitary-epidemiological requirements. The upward trend in the requirements for the physico-chemical and bacteriological composition of water is aimed at understanding and assessing the risks to human health resulting from the substances contained in the water. Water supplied to consumers must meet not only the appropriate quality parameters, but also quantitative ones. To meet these requirements, the following processes are used for the treatment of surface water: aeration and stripping, coagulation, sedimentation and flotation, filtration, ion exchange, chemical precipitation, activated carbon sorption, chemical oxidation, membrane processes and disinfection:

1. **Aeration and gas stripping** consists in introducing oxygen to water with the simultaneous removal of other gases dissolved in it, e.g. carbon dioxide, hydrogen sulfide, methane, etc. It affects the taste and smell of water. Aeration increases the content of dissolved oxygen in water, creating conditions for the oxidation of iron and manganese compounds and prevents the formation of a reducing environment conducive to rotting of water [2].
2. **Coagulation** – removes organic and inorganic colloidal particles, color, slow-settling suspensions and other micro-pollutants from the water. In this process, homonymous colloidal particles attract oppositely charged ions which neutralize their surface charge. With an excess of counterions, these particles gain opposite charge. All this causes the particles to immediately attract each other and destabilize the system. Some of the counterions are concentrated in the adsorption layer, and the rest are in the moving diffusion layer. The process of combining unstable colloidal particles into groups of particles called flocs (agglomerates, unstable aggregates) is called flocculation. The resulting agglomerates can be removed from the treated water in the processes of sedimentation, flotation and filtration [2].
3. **Sedimentation and flotation** – takes place in settling tanks, where high-density suspensions present both in the water before treatment, known as raw water, and after other unit processes, e.g. coagulation and chemical precipitation, are removed by the slow falling of particles. On the other hand, the flotation process removes particles with a density lower than that of water. Preceded by coagulation, this process can be used instead of sedimentation, eliminating light and slow-settling suspensions from the water. The sludge accumulated in the sludge chamber is periodically removed by means of movable scrapers [2].
4. **Filtration** – is one of the main technological processes used by waterworks to treat ground or surface waters. It consists in the flow of water through the filter bed, where contaminated suspensions are removed. There are two types of filtration, fast filtration which is applied after water treatment processes and slow filtration which is regarded as more effective due to accumulation of fast filtration process and biochemical processes occurring on filters [2].
5. **Ion exchange** – mainly used in the treatment of water intended for industrial purposes, and consists in removing dissolved substances from water, main-

ly phosphates and nitrates, methane nitrogen, metals and radionuclides, and ensures demineralization, softening and desalination of water [1].

6. **Chemical precipitation** – removes the hardness-inducing calcium and magnesium salts from the water [2].
7. **Activated carbon sorption** – consists in binding the removed pollutants on the adsorbent surface. It is used to remove dissolved organic compounds and their products of incomplete chemical oxidation, it lowers the content of pollutants affecting the color, taste and color of water [2].
8. **Chemical oxidation** – thanks to such oxidants as chlorine, ozone, chlorine dioxide or potassium permanganate, this process allows to, among other things, remove compounds that affect the taste and color of water, disinfect and decompose algae, oxidize organic refractory compounds, iron, manganese or protective colloids [1].
9. **Membrane processes** – these include processes such as reverse osmosis, electrodialysis, reverse electrodialysis, ultrafiltration and nanofiltration. They are mainly used for desalination of water, removal of color compounds, inorganic pollutants, bacteria and viruses. These processes involve the separation - by permeation through membranes with varying degrees of porosity – of liquid and gas mixtures. The membrane is a barrier for the components of the mixture undergoing treatment [3].
10. **Disinfection** – the process most often used in the final stage of water treatment before it is introduced into the water supply system. It consists in destroying pathogenic microorganisms remaining in the water after previous treatment processes and ensuring that the water in the water supply network is of good sanitary quality. Disinfection consists in adding chemical agents to the water, most often strong oxidants such as chlorine, chloramines, chlorine dioxide, or using physical factors such as ultrasound, UV rays [1].

As part of the preliminary processes for surface water treatment, gratings and microsieves are also used [3]:

1. **Gratings** – the first process of catching floating or suspended pollutants that could interfere with the proper operation of the pumps occurs on the grates. They cover the water intake windows.
2. **Micro-sieves** – it is a preliminary process in surface water treatment systems consisting in the elimination of microorganisms as well as organic and inorganic suspensions from the water. A micro-sieve is a drum covered with microfiber that is placed in a water tank, where water flows in and out straining through the microfiber and trapping dirt on the inside surface of the fabric.

Groundwater treatment usually consists of aeration, de-ironing, de-manganizing, removal of ammonium nitrogen and hardness, and final disinfection. Processes not previously described in the paper are discussed below:

1. **De-ironing** – removes iron ions from water by oxidizing a soluble divalent iron compound to a sparingly soluble divalent iron compound with a higher valence, which results in hydrated trivalent iron oxide. The simplest method of water de-ironing is aeration and filtering on multi-layer beds or two-stage filtration, where the oxidant is atmospheric oxygen. Other methods of this process include, among others, contact coagulation of water, ion exchange, stabilization of iron compounds [4].
2. **De-manganizing** – consists in the oxidation of water-soluble bivalent manganese ions to tetravalent, followed by their precipitation as insoluble manganese dioxide. Most commonly, filtration through a sand bed or a mixed sand and amber bed is used. Due to the insufficient efficiency defined by the norms of manganese concentration in water, active filter materials are used [5, 6].
3. **Removal of ammonium nitrogen** – consists in removing it from water by physical methods through stripping and ion exchange using clinoptilolite which has a high sorption and exchange capacity, as well as by chemical and biological methods. During the removal of ammonium nitrogen on clinoptilolite, significant amounts of post-regenerative leachate can be observed, therefore various methods of regenerant recovery are used, such as: ammonia stripping to the atmosphere, electrochemical and biological nitrification methods, and the denitrification method [4].
4. **Hardness removal** – a process that softens water through chemical precipitation, which removes the ions of the calcium and magnesium cations that make the water hard. Water softening by this method includes lime decarbonization, lime-soda precipitation and phosphate precipitation. Moreover, the ion exchange process is also used [4].

Table 1.
Waste characteristic form processes used in water treatment [8]

Process	Waste	Contaminants
Coagulation with iron or aluminium salts	Hydrated sludges and washings with a high aluminum or iron content.	As, Ba, Cd, Cr, Ni, Pb, Zn
Iron removal, manganese removal	Hydrated deposits of iron and manganese oxides.	Fe, Mn, As, Cd, Cr, Pb
Decorbanization with the precipitation method	Hydrated carbonaceous deposits	As, Ba, Cd, Cr, Pb, 226Ra
Adsorption	Used adsorbent	organic substances, As, Ca, Cr, Pb
Ion exchange	Brine	As, Ba, Cd, Cr, Se, 226Ra, F, NO_3-
Reverse osmosis	Brine	As, Cd, Cr, Se, 226Ra
Chemical oxidation, chlorine disinfection	-	THMs, chlorites, chlorates, bromates

3. TYPES OF SLUDGE POLLUTANTS

All the above-mentioned processes are the source of sludge, washings and sewage containing the removed pollutants at various stages of water treatment in water treatment plants, mainly during washing of filter beds, microsieves, cleaning of tanks and equipment. The sludge formed is a mixture of sludge water and solid particles and various types of chemicals used in the treatment processes. This poses threats resulting from the presence of various types of chemical compounds with toxic properties in the sludge and washings. Depending on the type and quality of treated surface and underground water, there are noticeable differences in the composition of sludge formed in the treatment process, e.g. in the amount and type of toxic compounds. The degree of the threat depends on the chemical composition of the sludge and on the method of its final neutralization, including storage. The chemical composition of the sludge depends mainly on [7]:

- the type and concentration of chemical compounds present in the treated water,
- type and doses of reagents used in the treatment process,
- cleaning effects determined by the type and amount of removed admixtures, as well as the type and concentration of intermediates and by-products of the reactions taking place in the treatment process.

All substances present in surface water and groundwater are separated from the water, accumulated and concentrated in sludge during treatment processes. Increased concentrations of such heavy metals as: Cr, Zn, Pb, Sb and Hg were found in the sludge from the treatment of surface waters. The organic pollutants present in the sludge include: monocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, pesticides and their metabolites, halogenated hydrocarbons, e.g., THMs formed in the process of water chlorination. The washings from groundwater treatment contain mainly iron and manganese oxides, which constitute 70-80% of the sludge mass [7].

Thus, the waters taken for water supply contain substances of natural and anthropogenic origin that must be removed in order for the water to be fit for human consumption. For this purpose, various technological processes mentioned above are used which generate waste. Its volume ranges from 2 to 5% of the volume of the treated water. The characteristics of waste generated in selected unit processes used in water treatment plants are presented in Table 1.

From Table 1, we can conclude that the most harmful pollutants are found in sludge formed during coagulation, ion exchange and decarbonization. The waste generated in water treatment plants, in addition to hydrated post-coagulation sludge, includes sludge after the aeration process, sludge formed in the sedimentation process and used water – mainly washings from washing filtration and adsorption beds, post-regeneration solutions (e.g., after cleaning membranes) and wastewater after rinsing devices used in plants. This sludge is a serious ecological problem due to the large volume and content of iron or aluminium hydroxide sediments, pollutants present in the treated water (mineral and organic substances, algae, protozoa and bacteria) and the added chemicals [8].

4. LEGAL REGULATIONS CONCERNING THE MANAGEMENT OF SLUDGE

The implementation of water and sewage management tasks is regulated by the provisions of both EU and national law. The Water Framework Directive 2000/60/EC of 23 October 2000 obligated the Member States to protect and use water resources in a rational way [9]. This directive organizes and coordinates existing European water legislation. Poland's accession to the structures of the European Union and the adaptation of Polish law in the field of water management and the operation of water treatment companies to its requirements drew attention to the issues of quantity, quality and method of processing sludge from water treatment.

According to the classification of waste specified in the Act of 14 December 2012 on waste, the sludge generated during water treatment should be treated as hazardous waste [10]. On the other hand, the ordinance of the Minister of Environment of 27 September 2001 on the waste catalog classifies sludge from water clarification (code 19 09 02) and sludge from water decarbonisation (code 19 09 03) as non-hazardous waste [11].

Regulation of the Minister of the Environment of March 21, 2006 on the recovery or disposal of waste outside installations and devices – permits the use of sludge from water clarification to clean and protect against water and wind erosion of the slope and top of a closed landfill or its part [12]. Pursuant to the above ordinance, it is not possible to use the sludge generated in water treatment processes to fill in the areas that have been adversely transformed, such as sinkholes, unexcavated open pits or the depleted parts of these pits.

Pursuant to the ordinance of the Minister of the Environment of February 26, 2009 (amending the ordinance on detailed requirements for the location, construction, operation and closure to which particular types of landfills should conform), sludge from water clarification may be used for the construction of slopes, including embankments and shaping the top of the landfill [13].

The conditions for the storage of sludge from water treatment systems at the landfill are specified in the Regulation of the Minister of Economy and Labor of January 8, 2013 on the criteria and procedures for accepting waste for storage at a given type of landfill [14]. Sludge from water clarification and water decarbonization can be stored in a non-selective manner [15].

Ordinance of the Minister of Environment of 19 December 2008 (amending the ordinance on the list of types of waste that a waste holder may transfer to natural persons or organizational units other than entrepreneurs, and acceptable methods of its recovery) allows the use of sludge from water decarbonisation (19 09 03) for liming acidic soils or using it as a building material. The natural use of this sludge must be in accordance with the principles set out in the regulations on the recovery process, in the amount not exceeding the possibility of using this waste on the area owned [16].

The natural use of sludge from water treatment, in any other way, is not specified in Polish law. So this is an interesting research area.

5. SELECTED METHODS OF VALORISATION OF SLUDGE

The waste (sludge and washings) generated in the water treatment process is a growing problem for water-producing companies. As mentioned earlier, the amount of sludge generated is between 2 and 5% of the treated water. The method of waste management is mainly determined by its physical and chemical properties and legal regulations.

The Waste Act of December 14, 2012 stipulates that waste that could not be prevented and whose negative impact on the environment must be limited, should be recovered prior to disposal [9]. Recovery is defined as the process by which waste is put to a useful use by replacing other materials that would otherwise be used to perform this function.

On the basis of the literature on the subject and many studies carried out both in Poland and abroad, it has been found, among others, that iron washings, as a source of large amounts of waste iron, can be used for:

- production of coagulants used in wastewater treatment [17-21],
- production of adsorbents used in wastewater treatment [22, 23],
- to improve sedimentation properties of activated sludge in wastewater treatment [24],
- oxidation of phthalates hazardous to human health, e.g., in the Fenton process, where they are a source of iron ions [25],
- binding of hydrogen sulfide generated in sewer networks [26].

Post-coagulation sludge can be used in numerous ways, for instance, as a secondary raw material for the production of e.g. cement or bricks, tiles, ceramic tiles and pipes (as a substitute for clay). Based on the research conducted by Luo et al. reported in [26], it appears that the ash containing aluminum compounds and silicates, which is added in the production of cement, and which is formed as a result of the combustion of water treatment sludge, has a higher durability and resistance to sulphate corrosion [12].

Due to the presence of heavy metals such as Cd, Pb, Hg, Ni, Cu, Cr or Zn in post-coagulation sludge, there is a limited possibility of using it in agriculture. Before using the sludge, it is necessary to test the trace content of these metals, so that it does not exceed, respectively, 20, 750, 16, 300, 1000, 500 and 2500 mg/kg of dry weight of the sludge [9].

It is possible to use compacted sludge for land reclamation, protection against water and wind erosion of slopes and the top surface of a closed landfill [8].

6. CONCLUSIONS

Sludge generated during water treatment is a significant problem. It was determined that the type of generated sludge depends on the applied process and its pollution degree depends on the type and quality of the water taken. The methods of sludge management are mainly determined by its physicochemical properties and chemical composition. The sludge can be used, for example, in construction as a material for the production of cement, bricks and roof tiles. In wastewater treatment technology, sludge can be used as an unconventional adsorbent, catalyst for reactions in oxidation processes, and to bind hydrogen sulphide from biogas produced during anaerobic fermentation of sewage sludge. The sludge can also be used to bind the hydrogen sulphide formed in sewer networks. The use of sludge for the reclamation of agricultural land is determined by the content of heavy metals in it, which is regulated by law.

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