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DEVELOPMENT OF PROCESSES FOR CAPITALIZATION OF SEWAGE SLUDGE ASH

PhD thesis - Summary

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„Development of processes for capitalization
of sewage sludge ash",

Contents of the summary of the PhD thesis

1. Sewage sludge from municipal wastewater treatment plants

Sewage sludge from municipal wastewater treatment plants can be considered an important resource in the context of increasing global demand for renewable and alternative energy [1]. Global interest in environmental issues has grown steadily, so that various concepts have been adopted, replacing the concept of sustainable development, which involves both the ecological side, the economic and social side. Proper and feasible management of sewage sludge from sewage treatment plants can be considered one of the biggest challenges in wastewater management [2].

Sludge can be used both in the energy sector (as an alternative resource in conventional electricity and heat production) and in agriculture (plant fertilizer) provided that appropriate quality products are obtained. Thus, various sewage sludge recovery methods are economically viable and environmentally friendly solutions compared to other conventional methods of waste management, such as sludge storage.

The stages of waste management require well-developed management and therefore sewage sludge management strategies must adapt to the European Commission's main concept of "reduction, reuse and recycling". The sewage sludge resulting from the urban wastewater treatment process is a biologically active mix that contains mainly water (88-99%), various microorganisms (pathogenic bacteria), organic and inorganic substances (heavy metals, phosphorus). A relatively small amount is recirculated in the technological process, but most is removed from the process [1]. In Europe, the amount of dry sludge resulting from the primary, secondary and tertiary stage is 90 g / person / day [2].

Within the European Union, the sewage sludge disposal directives have been replaced by directives promoting methods for stabilizing and recycling the sludge [3]. There are many legislative frameworks approved by the European Union regarding the management of this waste.

In this regard, Directive 86/278 / EEC [4] of 12 June 1986 encourages the use of sewage sludge in agriculture provided that possible harmful effects on soil, plants, animals and humans are prevented, therefore the use of untreated sludge is prohibited [2]. Operational Directive 91/271 / EEC [5], adopted on 21 May 1991, requires the monitoring and reporting of sewage sludge production for urban agglomerations. Article 14 of this Directive encourages the finding of ways to reuse the sewage sludge and also prohibits its disposal in the aquatic environment.

Framework Directive 2008/98 / EC [6] of 19 November 2008 regulates the recycling of waste, including sewage sludge. The Directive states that the main priority in waste management is the prevention of waste production, followed by the treatment of waste for reuse, recycling or recovery and, last but not least, its disposal [1]. Directive 2010/75 / EC [7] of 24 November 2010 updates and combines other directives on industrial emissions: Directive 2008/1 / EC [8] on integrated pollution prevention and control, Directive 2001/80 / EC [9] which limits the emission of pollutants into the air and Directive 2000/76 / EC [10] on the incineration of waste.

European directives are implemented through the following instruments [2]:

- legislation covering emission limits for various industries;
- implementation at national level of the maximum allowed concentrations in case of pollutant emissions;
- national economic instruments (pollution taxes);

Sludge is a waste that is generated from the three stages of the wastewater treatment process: the primary stage (mechanical stage), the secondary stage (biological stage) and the tertiary stage (nutrient removal stage). Sludge can also be considered a mixture of biomass generated by the processes of aerobic and anaerobic fermentation of organic and inorganic constituents (sand, metal oxides) [12]. The quality and physico-chemical characteristics of sludge depend on the quality of wastewater, such as treatment plant and the technology used for wastewater treatment. At the same time, in order to apply a management corresponding to the sludge management, its physico-chemical characteristics must be known [2].

2. Struvite

Fertilizers are essential for providing the neessary nutrients for plant growth and ensuring a rich harvest [13]. Fertilizers also play an important role in maintaining soil fertility, increasing crop yields and improving crop quality. However, a significant part of the amount of fertilizer is lost, leading to increased costs, waste of energy and environmental pollution. All of these are seen as challenges to maintaining the sustainability of modern agriculture [14].

The introduction of increasing amounts of fertilizers, water and pesticides in agriculture, along with new technologies, has led to important advances in modern agriculture in the last century [13]. Plant production per unit of agricultural land has greatly increased, this has allowed access to food for a growing population and promoted economic development [14].

On the other hand, the impact on the environment has been considerable. Continuous application of fertilizers and pesticides has resulted in increased eutrophication and surface water toxicity, groundwater pollution, air pollution, soil quality degradation and even changes in ecosystems. All these negative effects raise questions about the sustainability of modern agriculture [14].

The development of agriculture, without compromising the environment, can be achieved by:

- increasing the efficiency of fertilizer and water use;
- minimizing the amount of pesticides used;
- the use of an integrated management of agricultural systems;

Intensive agriculture is dependent on the use of chemical fertilizers. Increasing food production can not be achieved without increasing the amount of fertilizer used. This has led to the maintenance of global agricultural productivity in relation to population growth. This has also had a significant effect on rural economic development. However, the mismanagement of fertilizers, their excessive application, leads to an inefficiency that poses a threat to the environment. In order to avoid negative consequences for the environment, the efficiency of fertilizers must be increased [13, 15, 16].

There are many strategies that are used to increase the efficiency of fertilizers and eliminate the negative effects on the environment. These include: improving methods of applying fertilizer to the soil (localized application), precise fertilization, fertilization through irrigation systems and the use of environmentally friendly fertilizers [13, 15, 16].

Fertilizers divide into two categories:

- inorganic chemical fertilizers (nitrogen, phosphorus, potassium and complex fertilizers);
- organic fertilizers (compost, manure);

It was reported that to feed about 6 billion people in 2000 the consumption of nitrogen (N), phosphorus (P) and potassium (K) was 64.9, 25.9 and 18.2 kg / ha respectively. In 2014, when the population reached over 7 billion people, the consumption of nitrogen, phosphorus and potassium increased to 85.8, 33.2 and 20.4 kg / ha respectively [17, 18]. Moreover, the total amount of nutrient fertilizer ($N + P_2O_5 + K_2O$) was estimated in 2010 at 170.7 million tonnes, increasing to 175.7 million tonnes in 2011. Consumption of N, P and K is estimated to increase by 172%, 175% and 150% respectively compared to current consumption by 2050.

3. Glass fertilizers

Agriculture is a very important sector of the economy that plays a crucial role worldwide both as a food producer and as a field in which millions of people work. Since the 18th century, the practice of intensive agriculture has been possible due to the use of a higher percentage of arable land, irrigation, mechanization of agriculture and also due to the use of mineral fertilizers and crop protection through the use of pesticides [19, 20]. The use of chemicals to control pests, but also to increase productivity, has led on the one hand to an efficiency of the agricultural sector, but on the other hand has led to environmental pollution.

Mineral fertilizers are some of the most important products for the agricultural industry. In addition to providing nutrients for the soil, mineral fertilizers also have a role in regulating pH and increasing soil fertility. With the increase of the population over time, and therefore the need for food, the production and consumption of mineral fertilizers also increased. The evolution of the global consumption of mineral fertilizers in the period 2000 - 2020 is presented in table 3.1, noting a systematic increase in recent years.

Table 3.1. Global consumption of mineral fertilizers [21]

Years	**N (Mt)**	**P_2O_5 (Mt)**	**K_2O (Mt)**	**Total (Mt)**
2000/2001	80.8	32.4	22.2	135.4
2006/2007	97.4	38.1	26.9	162.4
2007/2008	100.5	38.4	28.9	167.8
2008/2009	97.7	33.7	23.4	154.8
2009/2010	102.2	37.6	23.7	163.5
2010/2011	104.1	40.6	27.5	172.2
2011/2012	107.8	40.6	27.7	176.1
2012/2013	108.1	41.6	29.1	178.8
2013/2014	110.4	40.3	30.2	180.9
2014/2015	111.8	41.3	31.5	184.6
2015/2016	112.9	41.8	31.8	186.5
2019/2020	119.2	45.7	35.3	200.2

At the same time, with the increase of the population and taking into account its growth trend, the area of arable land / person has decreased considerably. For example, it is estimated that in 2025 the area of arable land / person will be 56% smaller than it was in 1965 [22].

4. Adsorption

Rapid growth in the global human population, natural disasters and depletion of water resources due to climate changes, have led to a shortage of drinking water in various developing countries. In addition, the presence of heavy metal ions, such as: Pb^{2+} , Cr^{6+} , Mn^{2+} , Ni^{2+} , As^{5+}, Cd^{2+} , Hg^{2+} etc. which are extremely toxic pollutants, impose serious side effects on living organisms [23]. Heavy metals are considered metals that have a density greater than 4±1 g/ cm^3.

Segregation of unprocessed industrial and household waste containing contaminants has a negative effect on aquatic ecosystems by affecting the quality of surface and groundwater. In addition, prolonged excessive intake of heavy metal ions could damage the kidney, liver, brain and nervous system [24].

Various heavy metals are discharged into wastewater through effluents from various industries such as fertilizers, paints, metal fabrication, pigments, leather, batteries, alloy industry, electroplating, mining, etc. [25, 26]. At the same time, heavy metals can come from natural sources such as soil erosion, volcanic activity and the dissolution of rocks and minerals [152].

Due to the stability, high solubility and migration of heavy metals in aqueous environments this leads to the accumulation of non-biodegradable metal ions in the food chain at all levels by biomagnification, leading to heavy metal poisoning of living organisms [27]. Basically, heavy metals are absorbed by plants, thus entering the animal and human body through the food chain and negatively affecting their health and vital activity [28].

The electronic structure of the atoms of these contaminants determines their high reactivity, the tendency to form complex substances and therefore a high biochemical and physiological activity, which leads to a high impact on the environment and health. Therefore, it is necessary to treat wastewater contaminated with heavy metals before discharging them into the environment, in order to avoid negative consequences, such as contamination of drinking water [28]. Among the heavy metals present in wastewater, lead and copper are common.

Lead and copper can be removed from aqueous media using various conventional methods such as:

- chemical precipitation [29];
- solvent extraction [30];
- membrane filtration [31];
- ion exchange [32];
- electrochemical removal [33];
- coagulation [34];
- reverse osmosis [35];

However, these techniques have some disadvantages such as incomplete removal of metals, low efficiency, sensitive and expensive operating conditions.

5. Experimental results

The study presented in this thesis had the main purpose advanced research in the direction of developing studies aimed at processes of reuse and capitalization of ash obtained through incineration of sewage sludge from the waste water treatment plant in Deta, Timis, Romania.

Recovery of phosphorus from ash from sewage sludge obtained by struvite

- The main objective of this chapter was to evaluate the efficiency of phosphorus extraction from the ash obtained through calcination of sludge from the treatment plant in Deta, using as extraction agents two inorganic acids and an organic acid.
- The ash obtained by calcining the sludge at 850 ºC was characterized from a chemical and morpho-structural point of view. Chemical analysis indicated a phosphorus concentration of approx. 4.3%, other elements present in relatively high concentrations being Ca, Fe, Al.
- The X-ray diffraction spectrum revealed the presence of phosphorus in the ash in the form of PO_4^{3-} bound as $Ca_{10.1}Mg_{0.385}O_{28}P_7$. The FTIR spectrum confirmed the presence of phosphate, through the 1041 cm^{-1} band which was attributed to the PO_4^{3-} , PO_3^{3-} vibrations. Transmission electron microscopy also revealed the presence of phosphorus, through the mapping technique.
- The extraction efficiencies were in a wide range of values, being dependent both on the nature and concentration of the extraction acid, and on the liquid: solid

ratio. The comparative evaluation of the extraction efficiencies of phosphorus with the two inorganic acids, indicates that even at low concentrations, the extraction with sulfuric acid leads to better extraction yields compared to hydrochloric acid. The efficiencies achieved in the case of inorganic acids were significantly higher than those achieved using citric acid as an extraction agent, for the same value of the liquid: solid ratio. Thus, for a liquid:solid ratio value of 100:1, the maximum extraction yield reached with 0.15 M sulfuric acid was 96.3%, while for 0.40 M citric acid the extraction yield was 88.6%. In order to streamline the extraction process with citric acid at low values of the liquid: solid ratio, dual systems were used (mixtures of 0.1 M citric acid and 0.1 M sulfuric acid, in volumetric ratios between 0.1- 0.5, the volume of citric acid representing at least 50% of the total volume of solutions). Thus, the extraction performed with a mixture of sulfuric acid:citric acid in a volumetric ratio of 0.5 and a liquid: solid ratio of 40:1 led to an efficiency of 89.1%, very close to the value obtained by acid extraction 0.10 M sulfuric acid, 92.6%.

- To verify the accuracy and precision of the results obtained, three statistical methods were used: construction of Shewhart diagrams, use of double samples on different samples and control of the calibration curve by control samples of different concentrations. The processing and statistical interpretation of all quality control methods has proven that the experimentally determined results are accurate and reliable.
- The researches that are the subject of this chapter aimed the possibility of capitalizing the phosphorus from the extraction solutions from the sewage sludge ash in the form of a mineral fertilizer - struvite, through a chemical precipitation process.
- The extraction of phosphorus from the sewage sludge ash from was performed with sulfuric acid solutions of different concentrations at different values of the L:S ratio, following the conditions that allow obtaining a solution with the highest possible concentration of phosphorus, an important aspect for the process. chemical precipitation.
- From the analysis of the obtained results, it was chosen that the extraction solution be obtained under the conditions of using a 5% sulfuric acid solution, at an L:S ratio of 5:1, favorable conditions for an industrial scale process. Under these conditions, the extraction solution with a phosphorus concentration of 8.2 g / L was used to recover the phosphorus.
- Although the presence of toxic heavy metals such as Pb, Cr, Ni, Cd in the extraction solution may raise problems related to the purity and morphology of the products resulting from precipitation, a low concentration (<3 ppm) was highlighted, below the maximum limit allowed.
- Since the formation of struvite depends on the precipitation pH and the molar ratio Mg: N: P, in our studies values of Mg: P ratios of 1,2, 1,5, 1,8 and N:P = 1.2 and 1.5 were chosen as process parameters. Precipitation was performed at four pH values: 8.5, 9, 9.5 and 10.
- All compounds obtained by precipitation under the above conditions were characterized by chemical and morpho-structural analysis.
- The results of the chemical analysis allowed the calculation of the real molar ratio P: Mg: N which was compared with the theoretical molar ratio P: Mg: N = 1: 1: 1.
- Thus, for the set of compounds obtained under the values of Mg: P 1,2, 1,5, 1,8 and N: P = 1,2 at the four pH values, it was concluded that the pH precipitation

optimum which results in a compound whose molar ratio P: Mg: N of 1: 0.97: 0.83 was the closest to the theoretical ratio corresponding to pH 9, respectively to the molar ratio Mg: P = 1,5 and N: P = 1.2.

- X-ray diffraction analysis confirmed the results of the chemical analysis, the diffractogram of the precipitate obtained at pH=9 for values of molar ratios Mg: P = 1.5 and N: P = 1.2 highlighting struvite as the only crystalline phase.
- Similarly, for the set of compounds obtained under the values of the ratios Mg: P 1,2, 1,5, 1,8 and N: P = 1,5 at the four pH values, it was concluded that pH the optimum precipitation yield of a compound whose molar ratio P: Mg: N of 1: 1.08: 0.92 was the closest to the theoretical ratio corresponded to pH=10, respectively to the molar ratio Mg: P=1.2 and N: P=1.5.
- SEM images highlighted the presence of rectangular crystalline particles specific to struvite.

Recovery of ash in the synthesis of vitreous fertilizers

- Five compositions containing different amounts of ash embedded in the glass matrix were synthesized.
- The chemical activity and the efficiency of the fertilizers on the barley culture were studied for the considered glass compositions.
- Kinetic studies aimed at the solubilization of potassium, phosphorus and iron ions have indicated a favorable effect of fine granulation on the release of ions from the glass matrix.
- For the interpretation of the kinetic data, the intraparticle diffusion model was used. Two distinct stages of the ion solubilization process were highlighted: the first stage consists in the diffusion through the glass matrix, and the second consists in the diffusion at the particle boundaries. The intraparticle diffusion model for the solubilization of potassium, phosphorus and iron ions was calculated.
- The effect of the glassy fertilizers synthesized on the barley crop was evaluated using the following specific parameters: germination percentage, average total plant length and biomass. The results showed a favorable effect for plant development compared to the control sample. Based on the experimental data obtained, the C4 sample with a dose of 0.08 g/cm^2 was identified as the optimal sample.

Recovery of ash as an adsorbent material in the advanced treatment of residual effluents containing heavy metals (Pb^{2+} , Cu^{2+})

- In this chapter, the ability of ash to function as an adsorbent material in the process of retaining heavy metal cations from residual effluents was investigated. The heavy metals chosen as pollutants were Pb^{2+} and Cu^{2+} , the adsorption process being investigated for each metal (singular system) but also for both cations present in the solution (binary system).
- The efficiency of the adsorption process was studied taking into account the influence of the following factors: pH, ash dose, duration of the process and the initial concentration of Pb^{2+} and Cu^{2+} solutions.
- Although the adsorption capacity developed by the ash for Pb^{2+} was maximal at pH = 3, pH=6 was chosen as the optimal pH for subsequent adsorption studies. This choice was based on the fact that the simultaneous retention of the two cations is considered on the one hand, and on the other hand the fact that in relation to Cu^{2+} the ash has a maximum value of the adsorption capacity at

pH=6, pH at which the adsorption capacity of Pb^{2+} is slightly lower than at pH=3.

- The study on the influence of the adsorbent dose on the efficiency of the adsorption process identified as optimal the dose of 1 g/L.
- Kinetic studies performed in both single and binary systems indicated that the time required to reach the adsorption equilibrium was 210 min. The modeling of the kinetic data highlighted the fact that the adsorption process follows the pseudo-order-two kinetic model, for which the highest values of the correlation coefficients were obtained.
- The results obtained in modeling the experimental results indicated that the adsorption of Pb^{2+}, respectively Cu^{2+} from the solution faithfully follows the Langmuir isotherm, and therefore takes place in a monolayer system, on the energy-uniform uniform surface. This conclusion was also supported by the very good values of the correlation coefficients (0.999 for Pb^{2+} and 0.998 for Cu^{2+}, respectively). Moreover, no significant differences were found between the adsorption capacity obtained experimentally and that resulting from the modeling.
- In order to identify the mechanism of the adsorption process, investigations were performed on: comparative analysis of ash's diffractograms before and after adsorption; changes in SEM images of ash after adsorption; analysis of the affinity of ash in relation to Pb^{2+} and Cu^{2+} from the perspective of the electronegativity of the two cations and the size of the hydrated ionic rays; the concentration of Ca, Mg, K cations present in the solution after adsorption depending on its initial concentration; pH variation.
- From the correlation of all analyzed aspects, it was concluded that the adsorption process of Pb^{2+} and Cu^{2+} ions is controlled by chemosorption, and involves a cation exchange process. In addition, the alkaline properties of the ash and the neutralizing effect on aqueous solutions were highlighted.

The main original contributions resulting from the experimental research are:

- Morphological and structural characterization of the ash from the incineration of sludge from the wastewater treatment plant in Deta.
- Evaluation of phosphorus extraction efficiency using both simple and complex extractions by acid combinations.
- Evaluation of the quality of results using statistical control tools.
- The synthesis of struvite and the morphological and structural characterization of the obtained compounds.
- Obtaining vitreous fertilizers using ash and applying them on barley crops.
- Evaluation of the chemical activity of the obtained glasses and their efficiency as fertilizers.
- Use of ash as an adsorbent for water treatment with Pb^{2+} and Cu^{2+} content.
- Evaluation of the adsorption process performance in both single and binary system.
- Evaluation of the adsorption mechanism and performance of the adsorption process.

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