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RESEARCH ON THE PHYSICAL AND CHEMICAL PROPERTIES OF SEWAGE TREATMENT SLUDGE BIOCHAR AND ITS PREPARATION FOR WASTEWATER

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Abstract. Treatment and recycling of sludge waste have developed into a research focus in recent years. Today, nutrient recovery from wastewater and sludge has received much attention from regulators, academia, industry, and the general public. Institutions and governments around the globe are now seeking innovation to implement a "circular economy" for sewage sludge usage. The development of cost-effective and environmentally friendly disposal processes is necessary to meet political demands. In developing countries, common approaches to the treatment such as incineration and landfilling, cause unwanted secondary pollution. The study aims to determine sewage sludge biochar's physical and chemical properties and its preparation for wastewater treatment. The chosen chemical properties of sewage sludge biochar were electrical conductivity (EC), total organic carbon (%) content, physical properties were volatile solids, ash content, and also conducted phosphorus leaching experiment. It was determined that by increasing the pyrolysis temperature, the electrical conductivity (from 665 μS/cm to 277 μS/cm) and total organic carbon (from 29.03% to 17.25%) measurements decreased. By increasing the pyrolysis temperature, the ash content (from 50.07% to 69.45%), and volatile solids (from 53.61% to 74.55%) measurements increased.

Keywords: sewage sludge, biochar, chemical properties, physical properties.

Introduction

Sewage sludge is waste that can be used to make biochar. Current sewage biochar is being used for agriculture purposes, but cleaning and making safe fertilizer from this is complicated and takes a lot of energy. Using sewage biochar as an absorbent and biofilter for wastewater treatment.

Sewage sludge is an organic, solid, semisolid, or liquid by-product of the sewage treatment process. Sewage sludge is produced as a by-product (waste) during sewage treatment. With the expansion of wastewater collection systems in cities and other urbanized areas and the efficiency of wastewater treatment, the sludge generated during wastewater treatment is gradually increasing.

The amount of sewage sludge generated is 100,000 to 500,000 tons per year, which is the largest in developed countries, and neglecting its management can be a heavy burden (Grobelak et al., 2019). According to a report by the European Commission (2008), member states (26 EU) generated more than 10 million tonnes of dry sludge in 2008, with sludge volumes expected to raise to 13 million tonnes in 2020 (Grobelak et al., 2019). Lithuania's sewage sludge production is 82,000 tonnes per year, of which 60% is used for storage and landfill, 14% for agriculture, and 26% for composting (Praspaliauskas & Pedišius, 2017). In Lithuania, the infrastructure for the management of this waste was based on the amount of SS produced. According to Environmental Protection Agency's 2019 report, it consisted of 12 composting drying plants, 9 composting plants, and 2 sewage sludge drying plants (Aplinkos Apsaugos Agentūra, 2019). In 2017 the largest part of treated sludge is 48.3% – was used for fertilization and recultivation, 38.7% – compostable, 7.4% – disposed of in landfills, 5.2%– removed by other means and only 0.3% burned sludge (Aplinkos Apsaugos Agentūra, 2019). Since 2004, the country has rapidly developed WWT systems, applying the latest technology used by other EU members.

Treated sludge has been biologically, chemically, or thermally affected, stored for a long time, or affected by another process in such a way that its ability to ferment and the health risk posed by its use are reduced. In wastewater treatment plants, sludge is formed in mechanical treatment

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plants – primary precipitators and biological treatment plants – plants with activated sludge (Crini & Lichtfouse, 2019). The coagulation-sedimentation process in drinking water produces alum or iron sludge. It consists mainly of an inorganic matrix containing sand particles and a coagulant (Crini & Lichtfouse, 2019). Industrial wastewater residues in wastewater treatment plants are industrial sludges, many of which contain priority heavy metals and chemicals and are considered hazardous wastes upon treatment (Zhang et al., 2017). Sewage sludge generated in sewage treatment plants is a mixture of various inorganic and organic substances, also containing microorganisms and substances of various origins.

The composition of sludge, which contains numerous organic and inorganic compounds that positively and negatively impact the environment, determines its application and technology. Sludge consists of aggregates of constituents, including functional microorganisms and secreted extracellular polymeric substances, suspended in the effluent, and bio-aggregates in activated sludge tanks are called flocs.

An assessment of the extent of the problem shows that the volume of sewage sludge increased by 50% from 1992 to 2005, from 6.5 million tonnes of dry matter (DM) in 1992 to 9.8 million tonnes of DM in 2005 (Cieślik et al., 2015). In European Union, they account for an additional 1.1 million tonnes of dry matter. In this way, the total amount of SS produced by all European Union Member States (EU-27) in 2005 was 10.9 million DM-27 was slightly decreased (1%) (Cieślik et al., 2015). According to population estimates in the EU and elsewhere, the volume of untreated sewage sludge will continue to increase. Population growth and stringent demands on the quality of wastewater treatment will drive this increase. New wastewater treatment requirements have led more European Union countries to implement full-fledged wastewater treatment.

However, as a residue, sewage sludge can be used as an energy or resource source and can replace substantial amounts of materials/energy that must be produced from non-renewable resources with significant environmental impact. SS treatment and disposal practices are critical to environmental protection due to the levels of residual toxic metals, organic contaminants, and pathogenic microorganisms that can pose health problems and must be extracted. Meanwhile, they require large amounts of power (and associated environmental impacts), and the cost of SS treatment accounts for approximately 50% of the total operating costs of WWT (Brown et al., 2010). Sludge treatment processes have been found to account for 40% of total GHG from sewage treatment plants, and this number could be reduced if a CE approach were put in action (Brown et al., 2010).

Therefore, circular economy (CE) is a concept that is practiced in this field to address the sewage sludge problem. Researchers explore the linear and open nature of the modern economy, where natural resources provide input for production and consumption while acting as waste, explaining how it can affect the economy. The circular economy has emerged as the concept of an alternative to the "take-make-dispose" (linear) economic model and is founded on the following principles: Loop and Performance Economics and the Blue Economy (Geissdoerfer et al., 2017). As claimed by the Ellen MacArthur Foundation (EMF), a circular economy: is "an industrial system that recovers or regenerates through intent and design. We aim to eliminate the use of toxic chemicals that impede the use and eliminate waste through good design of materials, products and systems model" (Ellen MacArthur Foundation, 2015).

The study aimed to investigate the physical and chemical properties of sewage sludge biochar and its preparation for wastewater treatment.

1. Methodology

Samples of sewage sludge pallets were dried at a temperature of 100 °C at a constant mass. The moisture content of the obtained raw material was calculated to be 4.2±0.1% by weight loss (Januševičius et al., 2022). Biochar was produced from SS plates by pyrolysis in a tubular furnace (Januševičius et al., 2022). During the processes of pyrolysis, the nitrogen flow rate was chosen to be 2 liters/minute (Januševičius et al., 2022). 30 g of sewage sludge pellets were placed in a pot without an aluminum foil cover. Pyrolysis was performed at four different temperatures (300±1, 400±1, 500±1, and ±600±1 °C) for 2 hours.

The sewage sludge biochar characterized and properties were analyzed at the Technical University of Crete in the laboratories of the Environmental engineering faculty. Investigations were carried out from June 28, 2022, to August 5, 2022. The following characteristics and properties were determined using the methods described below.

To determine chemical properties like electrical conductivity (EC) it was taken these steps:

1. It was made of calcium chloride ($CaCl_2$) 0.005 M solution by weighing 0.2775 g of $CaCl_2$ and mixing it with 500 ml of deionized water. The solution was heated up to boiling temperature for 2 min and left to cool down.
2. It was chosen to make different pH values like 2±0.01, 4±0.01, 6±0.01, 8±0.01, and 10±0.01 to analyze not only electrical conductivity, and natural pH, but also biochar pH in $CaCl_2$ solution.
3. The $CaCl_2$ solution was adjusted to the chosen pH. 20 ml $CaCl_2$ of the solution was mixed with 0.06 g of SSB samples and initial SS without pyrolysis.
4. The mixtures were left for 24 hours in a shaker (Barnstead Thermolyne Big Bill Digital Orbital Shake Model 73625) at ~50 rpm.

To determine the total organic carbon (%) content of all sewage sludge biochar samples were weighed between 20 to 40 mg and put into a burning tray. The measurements were done with Shimadzu TOC-LCSH/CSN Standalone Model and Shimadzu SSM-5000A Solid Sample Module. First samples were oxidated at 900 °C and it was measured amount of CO_2 and converted to % of total carbon (TC) which has ±1% error. The next step was to take 90–100 mg of the sample, place it into Shimadzu SSM-5000A Solid Sample Module and mix it with 0.4 ml of phosphoric acid (H_3PO_4). After that, start the oxidation process at 200 °C. This way it was measured inorganic carbon (IC). To determine TOC it was used total carbon and inorganic carbon results using Equation (1):

$$TOC = TC - IC. \quad (1)$$

To determine the volatile solids content of all SSB samples (300 °C, 400 °C, 500 °C, and 600 °C) an initial sewage sludge was chosen to put approximal 1±0.002 g of sample into the crucible. The weight before and after biochar was placed in the crucible was noted. The samples were heated for two hours at 750±10 °C and 6 hours at 950±10 °C. Subsequently, the samples were weighted and volatile solids were calculated using Equation (2):

$$\text{Volatile solids}(\%) = \left[\frac{(w_2 - w_3)}{w_2}\right] \times 100, \quad (2)$$

where, w_2 is the weight of the air-dried sample, and w_3 is the weight of the sample after being heated at 950 °C.

The method used to determine the ash content of sewage sludge biochar was to open the lid of the crucible and heat it in a muffle furnace at 750±10 °C for 6 hours immediately after determining the amount of volatiles. After the crucible had cooled in a desiccator for 1 hour, it was weighed and then the sample heating process was repeated at the same temperature for 1 hour until the weight loss was less than 0.0005 g. To get the right number for sewage sludge biochar it only needed to be reaped twice. After that, the samples were raised and ash content was calculated according to Equation (3):

$$\text{Ash}(\%) = \left(\frac{w_4}{w_2}\right) \times 100, \quad (3)$$

where, w_2 is the weight of the air-dried sample, and w_4 is the weight of the residue after being heated at 750 °C.

The leaching experiment was performed in 250 ml Erlenmeyer flasks in shaker Barnstead Thermolyne Big Bill Digital Orbital Shake Model 73625 with flask clamps at 25 °C, at ~120 rpm to investigate the solubilization of phosphorus from sewage sludge biochar. 40 g of biochar samples and each was mixed with 80±0.5 ml water. The solutions were left to shake for 24 hours, after that the samples were filtered using a < 0.45 µm filter. Filtrate was measured to determine PO_4^{3-}-P concentration. The samples were filtered and the new 80 ml of water was filled, and the solutions were placed in a shaker for 24 hours. The process was repeated 9 times in total.

To measure PO_4^{3-}-P concentration the method used was:

1. The analytic solution was made using: 25 ml of sulphuric acid (H_2SO_4), 7.5 ml of ammonium molybdate, 2.5 ml of potassium antimony tartrate, and 15 ml of ascorbic acid.
2. 25 ml of sample was mixed with 4 ml of analytic solution and left for 15 min. The solution changes color from clear to blue and the intensity of the color shows the number of phosphates in the solution.
3. The samples were analyzed using a spectrophotometer at a wavelength of 880 nm. The ABS results were calculated to PO_4^{3-}-P concentration using the calibration curve equation.

2. Results

Electrical conductivity (EC) of sewage sludge biochar was measured, the results are presented in Figure 1. The highest amount of EC had been measured in initial sewage sludge biomass, as expected untreated sewage sludge has not only a lot of organic compounds but also a lot of salts dissolved into after during the measuring process.

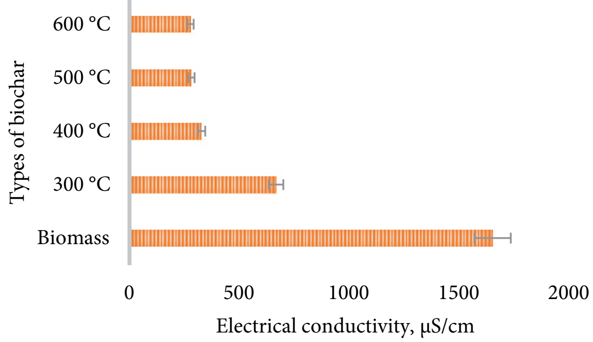

Figure 1. The sewage sludge biochar measured electrical conductivity, µS/cm

Comparing EC of biochar samples, the highest number had been recorded with SSB of 300 °C (665 µS/cm) and the lowest value was with SSB of 600 °C (277 µS/cm). This shows that the higher the temperature of pyrolysis, the less inorganic salts have been left in biochar. Other researchers had determined that usually, the EC of biochar can be between 40 µS/cm and 5420000 · 104 µS/cm (Smider & Singh, 2014). This huge difference shows that EC depends on the raw material of biochar. Also, from this research results in it could be stated that EC depends also on biochar pyrolysis temperature, the higher the pyrolysis temperature the lower EC, and the lower the pyrolysis temperature the higher EC.

Figure 2 shows the comparison of total organic carbon, inorganic carbon, and total carbon between different types of sewage sludge biochar and initial sewage sludge biomass. The SS biomass compared with SSB had decreased in total organic carbon from 29.03% to 17.25%, as shown in Figure 3. The highest total organic carbon was found not in sewage sludge biomass (26.01%), but in sewage sludge biochar of 300 °C (26.03%). The lowest TOC value showed sewage sludge biochar of 600 °C (17.25%). Some reports agree with the results of this research that total organic carbon content decreases while increasing

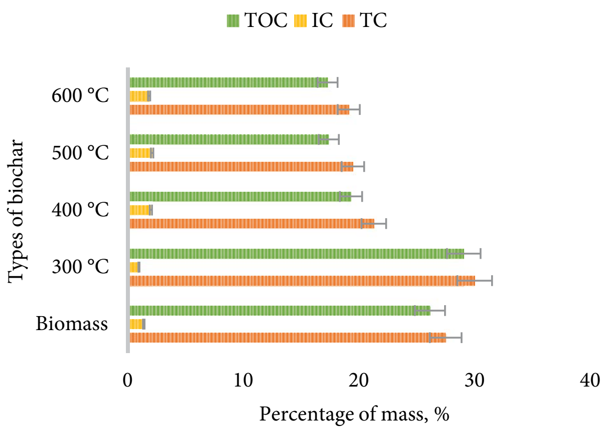

Figure 2. The sewage sludge biochar measured total organic carbon, inorganic carbon, and total carbon

the pyrolysis temperatures (from 300 °C to 600 °C) (Raj et al., 2021).

Volatile solids show an approximate amount of organic matter present in solids which means that the results from this research show that by increasing pyrolysis temperature the amount of organic matter reduces. Because the lowest amount of volatile solids was determined to be at 300 °C (53.61%), the highest amount was found at 600 °C (74.55 %).

According to Sadaka et al. (2014) study it was found that biochar volatile solids decreased by increasing pyrolysis temperatures from 300 °C to 400 °C. They reported that fast pyrolysis-produced biochar contains 16.4% volatile solids, and gasification-produced biochar contains only 10.3% volatile solids which means the pyrolysis process is better for reducing organic matter from materials. Another study also agrees with the statement (Yang et al., 2017). In this research, the results show the opposite effect, increasing the pyrolysis temperature also increases the number of volatile solids in biochar (Figure 3). This could be happening because the biochar is made from sewage sludge which could contain a lot of volatile compounds and the wastewater in the district of Vilnius could be contaminated more than it was thought.

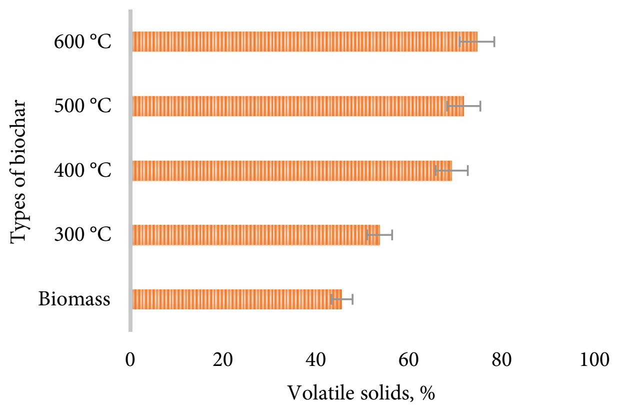

Figure 3. The sewage sludge biochar measured volatile solids (%)

The investigated sewage sludge biomass and biochar were characterized by high ash content ranging from 42.21% for sewage sludge biomass and from 50.07% to 69.45% for sewage sludge biochar (Figure 4). A similar trend was also observed with volatile solids (%), with an increase in the temperature of pyrolysis leading to a gradual increase in the mass of volatile solids.

This indicates an increase in ash content compared to the starting material. In this research, the value of the ash content parameter increased with increasing pyrolysis temperature. Other research done with biochar has shown that it is a common thing for biochar characteristics (Zielińska et al., 2015). In this connection, non-volatile mineral constituents are concentrated in the ash and volatile organic decomposition products are removed. This is confirmed by the fact that the mineral fraction was the predominant fraction in both the initial SS and the biochar. The ash content of sludge-based biochar is much higher compared to biochar made from other materials (Lu et al., 2013; Novak et al., 2009; Smider & Singh, 2014).

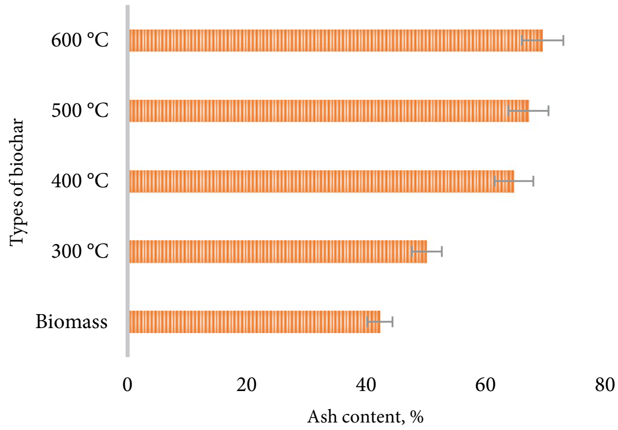

Figure 4. The sewage sludge biochar ash content (%)

For further biochar application in the removal process of phosphates, the leaching experiment of phosphate (PO_4^{3-}-P) was conducted. This characterization is important for biochar because leaching out substances in the water could lead to further pollution or increased concentrations of elements. The results of the leaching experiment and phosphate concentration in the water are shown in Figure 5. Daily concentrations of PO_4^{3-}-P (mg/l) are shown for all sewage sludge biochars.

The highest amount of PO_4^{3-}-P was released from sewage sludge biochar of 500 °C (sum for all amounts of water – 0.1727 mg/g), this biochar during all the measuring times had shown the highest values. The lowest released was from sewage sludge biochar of 600 °C (sum for all amounts of water – 0.0899 mg/g).

The leaching concentrations of the constituents were affected by the contact time because the concentration of phosphates had no significance compared to the same type of biochar. This property of sewage sludge biochar would likely be considered to be used in agriculture as

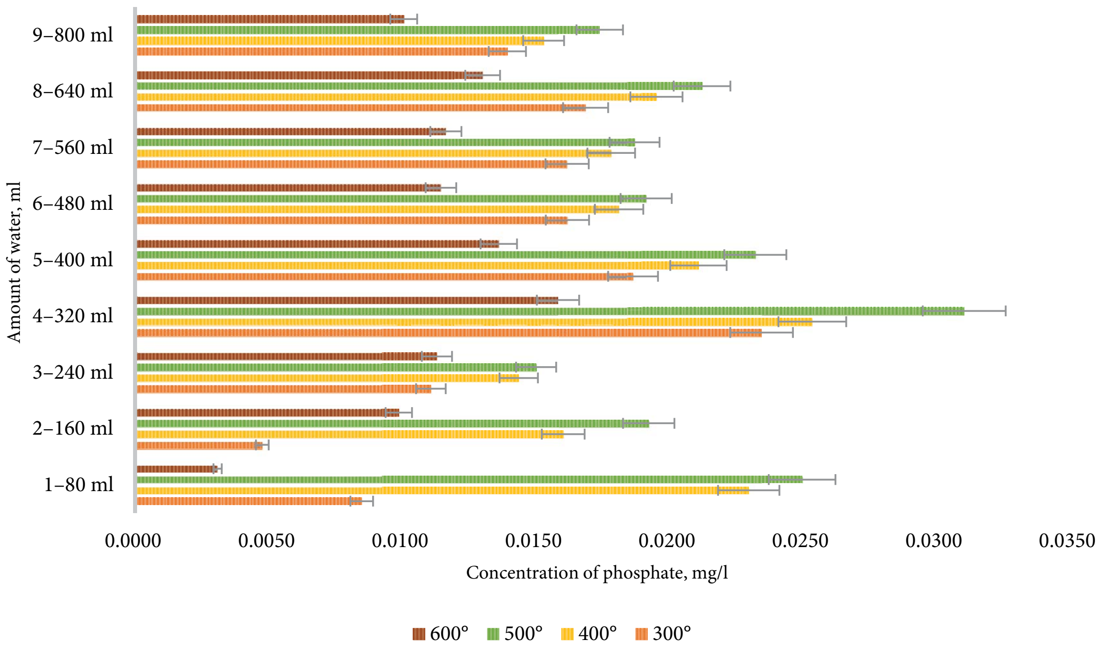

Figure 5. Daily concentrations of PO_4^{3-}-P (mg/l) during leaching process

phosphorus fertilizer. But it also needs to be considered the chemical composition of sewage biochar would contain heavy metals, and organic or volatile compounds. One of the other opportunities for sewage sludge biochar would be used in wastewater treatment as an adsorbent. This requires further research.

Conclusions

1. Electrical conductivity, total organic carbon, ash content, and volatile solids retention were primarily affected by the pyrolysis temperature. By increasing the pyrolysis temperature, the electrical conductivity (from 665 μS/cm to 277 μS/cm) and total organic carbon (from 29.03% to 17.25%) measurements decreased. By increasing the pyrolysis temperature, the ash content (from 50.07% to 69.45%), and volatile solids (from 53.61% to 74.55%) measurements increased.
2. By determining the characteristics of sewage sludge biochar shows the perspectives of the possible usage of this type of biochar in the agriculture and energy sector.
3. Future research is also needed to investigate the possibilities of a new way to use sewage sludge biochar for ecological, and economical benefits by making it back to the wastewater treatment process.

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NUOTEKŲ DUMBLO BIOANGLIES FIZIKINIŲ IR CHEMINIŲ SAVYBIŲ TYRIMAI IR PARUOŠIMAS NUOTEKŲ VALYMUI

J. Paulionytė, R. Vaiškūnaitė

Santrauka

Dumblo atliekų apdorojimas ir perdirbimas pastaraisiais metais tapo mokslinių tyrimų centru. Šiandien maistingųjų medžiagų atgavimas iš nuotekų ir dumblo sulaukė daug akademinės bendruomenės, pramonės ir plačiosios visuomenės dėmesio. Institucijos ir vyriausybės visame pasaulyje dabar ieško naujovių, siekdamos įgyvendinti nuotekų dumblo naudojimą žiedinėje ekonomikoje. Ekonomiškai efektyvių ir aplinką tausojančių šalinimo procesų plėtra yra būtina siekiant patenkinti politinius reikalavimus. Besivystančiose šalyse įprasti panaudojimo metodai, tokie kaip deginimas ir šalinimas sąvartynuose, sukelia nepageidaujamą antrinę taršą. Darbo tikslas – nustatyti nuotekų dumblo bioanglies fizines ir chemines savybes bei paruošimą nuotekų valymui. Pasirinktos nuotekų dumblo bioanglies cheminės savybės – elektros laidumas, organinės anglies kiekis, o fizikinės savybės – lakiosios kietosios medžiagos, pelenų kiekis, taip pat atliktas fosforo išplovimo eksperimentas. Nustatyta, kad didinant pirolizės temperatūrą sumažėjo elektros laidumas (nuo 665 μS/cm iki 277 μS/cm) ir organinės anglies kiekis (nuo 29,03 % iki 17,25 %). Padidinus pirolizės temperatūrą, padidėjo pelenų kiekis (nuo 50,07 % iki 69,45 %) ir lakiųjų kietųjų dalelių kiekis (nuo 53,61 % iki 74,55 %).

Reikšminiai žodžiai: nuotekų dumblas, bioanglis, cheminės savybės, fizinės savybės.