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PINE-DERIVED BIOCHAR AS OPTION FOR ADSORPTION OF CU, ZN, CR, PB, NI AND DECREASING OF BOD_5 IN LANDFILL LEACHATE

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Abstract. Landfill leachate is a highly toxic and hazardous form of wastewater due to its complex composition characteristics, e.g. ammonia, metals, organic compounds. Landfill leachate treatment technologies, such as flotation, coagulation/flocculation, precipitation, oxidation, micro-, ultra-, nanofiltration, reverse osmosis, are too expensive, because they require frequent regeneration of the media or generate secondary brine wastes that may pose a disposal problem. In the present study removal of Zn, Ni, Cr, Pb, Cu from Kazokiškės landfill leachate was studied. Kazokiškės landfill is the main site for disposal of Vilnius region municipal wastes. Operator of the landfill is interested in the alternative ways for the primary treatment of the landfill leachate for reducing the load on the expensive reverse osmosis. One of the proposed options for the primary landfill leachate treatment was adsorption by biochar. Due to the high specific surface area, well-developed porous structure and surface functionality biochar has been used as low-cost adsorbent for adsorption of PTEs from aqueous solutions. Biochar was produced from Scots pine *(Pinus sylvestris* L.*)* trunk wood (after debarking) by pyrolysis at the highest heating temperature of 700 °C for 45 min in the low-oxygen environment. Laboratory analysis showed that PTEs, such as Zn, Ni, Cr, Pb, Cu, were present in the landfill leachate before water treatment plant. Thus, the aim of the study was to evaluate PTEs (Zn, Ni, Cr, Pb, Cu) removal efficiency by adsorption by pine-derived biochar. Factors, affecting adsorption efficiency, such as biochar particle size (1, 2.5, 4, 5 mm) and dosage of the biochar (1.01, 3.5, 6.05, 9.45, 13.25, 17.82 g/100 ml of leachate) were studied. Effects of the biochar on pH of the landfill leachate, BOD_5, PTEs adsorption were analyzed. The findings showed that optimal parameters for decreasing of BOD_5 and retention of Cr and Pb were particle size 1 mm and dosage 6.05 g/100 ml of leachate and 1 mm and more than 13.25 g/100 ml of leachate, respectively. No positive effect on Cu and Zn was observed.

Keywords: woody biochar, adsorption, metals, landfill leachate, BOD_5.

Introduction

Water pollution is a serious problem for the entire world, because it threatens the health for humans, plants and animals. Metallurgical and wastewater treatment plants, coal combustion processes, transport, using of phosphorous and mineral fertilizers create problem of water contamination with potentially toxic elements (PTEs). Municipal activities produce huge amounts of wastes, which require permanent disposal. For 2015, municipal waste generation totals vary considerably, ranging from 789 kg per person in Denmark to 448 kg per capita in Lithuania (Eurostat 2015). Landfill is the major solid waste disposal option for most countries. Even though more waste is being generated in the EU-27, the total amount of municipal waste landfilled has diminished. During 1995–2015, the total municipal waste landfilled in the EU-27 fell from 144 mln t to 61 mln t. As a result, the landfilling rate compared with municipal waste generation, in the EU-27 dropped from 63.8% in 1995 to 25,3% in 2015.

Solid waste in a landfill is degraded through aerobic and anaerobic processes. Stabilization of the wastes is a very complex and variable event due to the site-specific characteristics of each landfill. The degradation products generated from the degradation process include leachate and gas. Landfill gas is generated due to the anaerobic biological degradation of organic material. Leachate is formed from the contact of water with refuse. Landfill leachate contains high concentration of biodegradable and non-biodegradable PTEs, e.g. ammonia nitrogen, chlorinated organic and inorganic salts etc (Azmi *et al.* 2016). Biological oxygen demand (BOD_5) characterizes the pollution level of wastewaters.

The Kazokiškės landfill has been the main site for disposal of Vilnius region municipal wastes for 10 years. It is situated in the Kazokiškes village in north-eastern part of Elektrėnų municipality. The landfill is 3.5 km north from the city Vievis, 1.7 km east of Zelva lake and 1.6 km south of the river Cielgio. River Neris is flowing 4 km to the north-east and Kernavė town – 8 km to the north. The exact coordinations according to LKS-94 system are 6074802, 552834. Total landfill site area – 30.16 ha, area of waste deposit of 27.1 ha is divided into 6 sections. The waste is deposited in section No 2 of an area of 6.0 ha. Owner and landfill operator is JSC VAATC (Vilnius County Waste Management Center). Annually 339 900 t of waste is disposed.

The leachate content of PTEs is strongly influenced by the composition of the waste deposited in the landfill and the processes in the body of landfill. As a result of physical, chemical and microbiological processes, PTEs from waste are transported to leachate. Landfill leachate PTEs content is directly dependent on the climatic and meteorological conditions of the site, e.g. the rainfall intensity and the on-going activities on the territory of landfill: garbage sorting, technology of tipping and use of depositing site etc (Kuusik *et al.* 2014).

Our experimental data of Kazokiškės landfill found BOD_5 600 mg/l, Zn 0.21 mg/l, Ni 0.34 mg/l, Cr 1.39 mg/l, Pb 0.028 mg/l, Cu 0.044 mg/l. The data kindly procured by the staff of Kazokiškės landfill, indicated the following values after reverse osmosis treatment of landfill leachate: BOD_5 22.4 mg/l, Zn 0.04 mg/l, Ni 0.007 mg/l, Cr 0.014 mg/l, Pb 0.001 mg/l, Cu 0.003 mg/l. In spite of values of leachate treated by reverse osmosis, operator of the landfill was interested in the alternative ways for the primary treatment of the landfill leachate for reducing the load on the expensive reverse osmosis. One of the proposed options for the primary landfill leachate treatment was biochar.

Conventional wastewater treatment methods (e.g. reverse osmosis, aerobic and anaerobic biological treatment, ozonation, may have some significant disadvantages, like incomplete removal, expensiveness due to excessive energy, manual labor, operations and maintenance requirements, production of toxic sludge (Renou *et al.* 2008; Khurma *et al.* 2013). Adsorption of PTEs by porous sorbents is a promosing option for wastewater treatment. Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as chitosan, zeolites (Babel, Kurniawan 2003). One of the low-cost natural sorbents based on the principles of sustainable development is biochar. In recent years, many studies have been devoted to investigate the application of biochar for PTEs removal from aqueous solutions (Tan *et al.* 2015; Inyang *et al.* 2016). The functional groups on the surface of biochar, such as hydroxyl, carboxyl, ether, amide, amine, alkayl, alkyne, alkine and carbonyl are responsible for adsorption of PTEs from wastewater. The atomic ratios such as H/C (aliphatic), O/C and N/C (polar index) are related to the specific properties of the biochar (Ahmed *et al.* 2016). When compared with activated carbon (AC), biochar could be produced from wastes (Baltrėnaitė *et al.* 2016a) at lower temperatures in a shorter time period (Ahmad *et al.* 2014) and costs 3 times lower (alibaba.com). The weak side of the biochar is the lower microporosity and surface area in comparison to activated carbon.

According to the European Biochar Certificate, lignocellulosic feedstock is the most valuable raw material in terms of its accessibility and waste management reasons. Sawdust of poplar, willow, fir, oak and black locust wood can adsorb the following PTEs in the indicated order Cu>Ni>Zn at particle size of 1 mm (Šćiban, Klašnja 2004). *Pinus sylvestris L.* woody biochar was used in biofiltration systems for removal of volatile compounds from the air (Baltrėnas *et al.* 2015, 2016). It was noted that removal efficiencies of Pb and Cd by oak bark biochar are comparable to that of commercial activated carbon, and biochar produced from wood can effectively adsorb Cu and Zn in aqueous solutions (Inyang *et al.* 2016). Properties of wood, that can influence the adsorption of PTEs, include lignin, water content, mineral composition, morphology and pore structure (Baltrėnaitė *et al.* 2016b, 2016c).

Adsorbent dosage can influence efficiency of adsorption. Previously the optimum activated carbon dosage 7 g/100 ml for removal color, COD and NH_3-N was found (Azmi *et al.* 2016). The same dosage showed the highest removal of the same constituents in landfill leachate by Sea mango based activated biochar with KOH (Shehzad *et al.* 2016).

The aim of the study was to investigate the effect of pine-derived biochar on the adsorption of Cu, Zn, Cr, Pb, Ni from landfill leachate. Such parameters as particle size and adsorbent dosage were altered.

Methodology

Biochar production

Due to local availability, cost-effectiveness and the prevalence of coniferous trees in Lithuania, pine was selected for biochar production. As regards biochar production, a method described in the work by Mancinelli *et al.* (2016) was followed. Air dried feedstock was placed in open crucibles, weighed, and wrapped in aluminium foil in order to create an oxygen-limited environment. An E5CK-T muffle furnace was used with a heating rate of approximately 10 °C/min until the desired pyrolysis temperature of 700 ± 5 °C was reached. The fast pyrolysis process was performed for 45 min under atmospheric pressure. At the end of the production process, the samples were left to cool in the muffle furnace overnight.

The obtained biochar was grounded after being cooled down to ambient temperature (20 ± 3 °C), and a 1–10-mm-diameter fraction was separated by sieves (Retsch, Germany). Biochar yield (%) was calculated according to as follows:

$$Y_{bc}=\frac{W_2}{W_1}\times 100\% \quad (1)$$

where W_1 – the dry mass of the feedstock, g; W_2 – the dry mass of biochar, g.

Physical properties of biochar

Skeletal density (analogue VDLUFA-Method A 13.2.1) was measured in accordance with EBC guidelines (EBC 2012). The samples of biochar were filled into a graduated cylinder and the mass was determined by weighting. The density in kg/m^3 was calculated from the mass and the volume of the sample.

The morphology and specific surface area of pine biochar were determined at Scientific Institute of Thermal Insulation of Vilnius Gediminas Technical University using scanning electron microscope and mercury porosimeter Quantachrome Poremaster PM-33–12, respectively.

Chemical properties of biochar

pH was determined by an instrumental method using a glass electrode in a 1:5 (volume fraction) suspension of 0.4 mm fraction of the biochar in deionized water (Komkienė, Baltrėnaitė 2016). After shaking the suspension for 1 h and after allowing deionized water to stand for 1 h, the pH was measured using Mettler Toledo Seven Multi pH meter (Germany).

Cation exchange capacity (CEC) was determined using ammonium acetate (Komkienė, Baltrėnaitė 2016). Twenty-five grams of biochar was allowed to stand overnight after being thoroughly shaken with 125 ml of 1 M NH_4OAc. The biochar was transferred in filter paper-fitted Buchner funnel. The biochar was gently washed four times with 25 ml additions of NH_4-OAc. The leachate was discarded and the biochar was washed with eight separate additions of 95 % CH_3CH_2OH to remove excess saturating solution. The adsorbed NH_4 was extracted by leaching the biochar with 1 M KCl. The biochar was removed and the leachate was transferred to a volumetric flask to dilute to 250 ml volume with additional 1 M KCl. The concentration of NH_4–N was determined in the KCl extract by colorimetry (from composed ammonia calibration curve by measuring absorption intensity at k = 400 nm with photocolorimeter in 1 cm length cells, concentration of NH_4–N was calculated using Nessler method. Also NH_4–N was determined in the original KCl extracting solution (blank) to adjust for possible NH_4–N contamination in this reagent. Cation exchange capacity was calculated using equation 2:

$$CEC=\frac{NH_4N_{inextract}-NH_4N_{inblank}}{14} \quad (2)$$

where CEC – cation exchange capacity, $cmol_c$ /kg; $NH_4N_{in\ extract}$ – ammonium ion concentration in the extract, mg/ l; $NH_4N_{in\ blank}$ – ammonium ion concentration in the blank, mg /l.

Total carbon (TOC) was determined according to Komkienė and Baltrėnaitė (2016) using Total Organic Carbon Analyzer TOC-V (SHIMADZU, Japan). Samples of biochar were dried at room temperature, sieved through a 2-mm sieve, crushed, and homogenized. 20 mg of each biochar sample weighed in the combustion cell was placed in the combustion chamber.

Column test set-up

The solutions used is landfill leachate taken from Kazokiskės landfill in Vilnius region, Lithuania. Column test was used for treatment of landfill leachate with biochar of different particle size and dosage.

Six experimental columns in compliance with ISO 21268–3 were made of organic glass with internal diameter of 43 mm and height of 50 cm and fitted with metal filters at the bottom in order to prevent the grains passing through (Fig. 1). Port between the columns and wooden frame had the options "opened/closed" to regulate velocity of outlet flow.

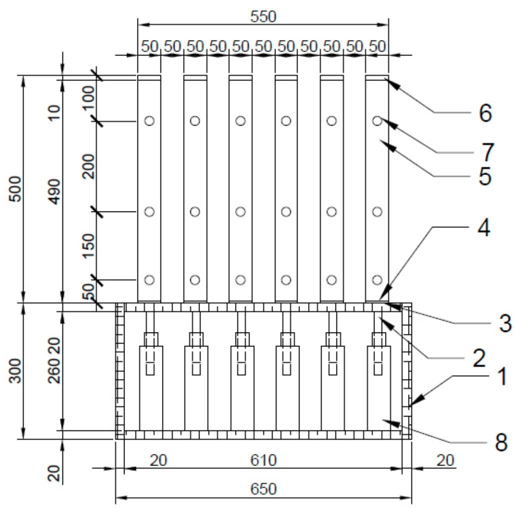


Fig. 1. Stand for a column leaching test: 1 – wooden frame, 2 – tap, 3 – plastic filter, 4 – metal mesh, 5 – organic glass cylinder, 6 – plastic lid, 7 – channel with rubber tube, 8 – 1000-mL HDPE bottle

Biochar was separated into different particle sizes of 1, 2.5, 4, 5 mm. Each column was filled with different dose of biochar: 1.01, 3.5, 6.05, 9.45, 13.25, 17.82 g/100 ml. Then landfill leachate was applied to columns temperature (23 ± 2 °C in laboratory). Duration of each experiment was 100 min and velocity of treated leachate going from was 3 ml/min.

Concentration of PTEs in landfill leachate

For the purpose of the determination of concentrations of Cu, Cr, Zn, Ni, Pb in landfill leachate, it was poured into 50-ml flask. The concentrations of PTE in the samples were determined by the atomic absorption spectrophotometer Buck Scientific's 210VGP.

BOD_5 was measured with BOD sensor system with magnetic shaking (VELP Scientifica) after 5 days. The limit of detection is up to 999 mg/l.

Quality assurance and statistical analysis

Each analysis was prepared and analysed in duplicates. The measurements were carried out three times and the average of the results of measurement errors was calculated. The statistical analysis was performed using Excel program. The results of arithmetic mean values with values of relative errors were presented in graphical expression of the results. The standards of calibration were used to calibrate devices in each year. The quality of experiments was assured by blank samples such as deionized water (for NH_4–N) and KCl (for pH).

Results

Physico-chemical properties of biochar

Physico-chemical characteristics of the pine biochar are summarized in Table 1. According to diameter (d), pores are classified as micropores (d < 2 nm), mesopores (2 nm < d < 50 nm) and macropores (d > 50 nm) (Lehmann, Joseph 2015). Mercury intrusion porosimetry (MIP) is a suitable technique to describe meso- and macroporous structure, in our case pores with diameter higher than 6.449 nm. Smaller-diameter pores were investigated by N_2 adsorption at low temperatures.

Different conditions of pyrolysis process (such as temperature and duration of thermal treatment) and the wood

biomass type influence the reduction in mass, i.e. the weight of dry Scots pine biomass decreased in 4.63 in the production of biochar under fast pyrolysis conditions. When the heat treatment temperature was (700 ± 5) °C, the biochar yield reduced more than at conditions of slow pyrolysis due to increase of aromatization of biochar.

The average moisture content of fresh wood depends on species and seasonal variations. Moisture content of Scots pine sample was 49.11%.

Pyrolysis conditions influence adsorptive characteristics of the biochar, e.g. specific surface area and cation exchange capacity (CEC). With the increase of temperature volume of micropores increases, consequently, specific surface area of the biochar increases. BET Specific surface area of activated carbon from sugarcane bagasse was in 9 times higher (99.95 m^2/g) than of biochar in present paper (10.4 m^2/g) (Azmi *et al.* 2016). On the contrary, CEC decreases with the temperature, that indicates less polarity of the biochar.

Effect of biochar on pH of the landfill leachate

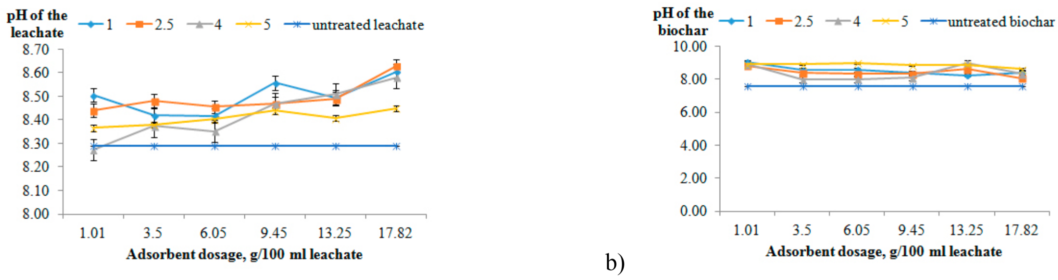
Due to high pH of Scots pine biochar, pH of landfill leachate slightly increased (Fig. 2). The most significant increase in pH was noticed in the biggest biochar dosage of 17.82 g/100 ml of landfill leachate. Highly alkaline biochar of smaller particle size (1 and 2.5 mm) increased pH of landfill leachate more than biochar of bigger particle size. This could be explained by bigger contact surface of smaller particles with landfill leachate media.

As the solubilities of the metals are minimized in the pH range of 8.0–11.0, Cu, Cr, Zn, Pb could be removed from landfill leachate through precipitation (Fu, Wang 2011). Moreover, pH of the biochar increased after the contact with landfill lachate. No dependency on biochar dosage was observed. pH of the biochar increased from 7.52 to 9 at the particle size of 5 mm.

Table 1. Physico-chemical characteristics of the biochar, the mean value

Biochar	Temperature of pyrolysis (°C)	Time of pyrolysis (min)	Yield, %	Skeletal density, g/cm^3	Apparent density, g/cm^3	TOC, %	Specific surface area (m^2/g)	Porosity, %	pH	CEC (cmolc/kg)
Pine BC	700 (±5)	45	21.6	1.23	0.499	95.8 ± 0.01	10.4	77.3	7.52 ± 0.01	2.40 ± 0.21

BC – biochar, TOC – total organic carbon, CEC – cation exchange capacity



a) b)

Fig. 2. Changes in pH after experiment of a) landfill leachate, b) biochar. Values are mean ± SD

Effect of biochar on BOD_5 of landfill leachate

Results on BOD_5 decrease are presented in Fig. 3.

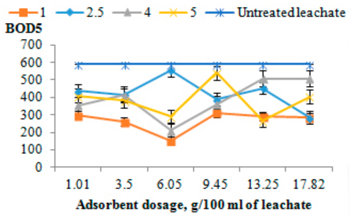
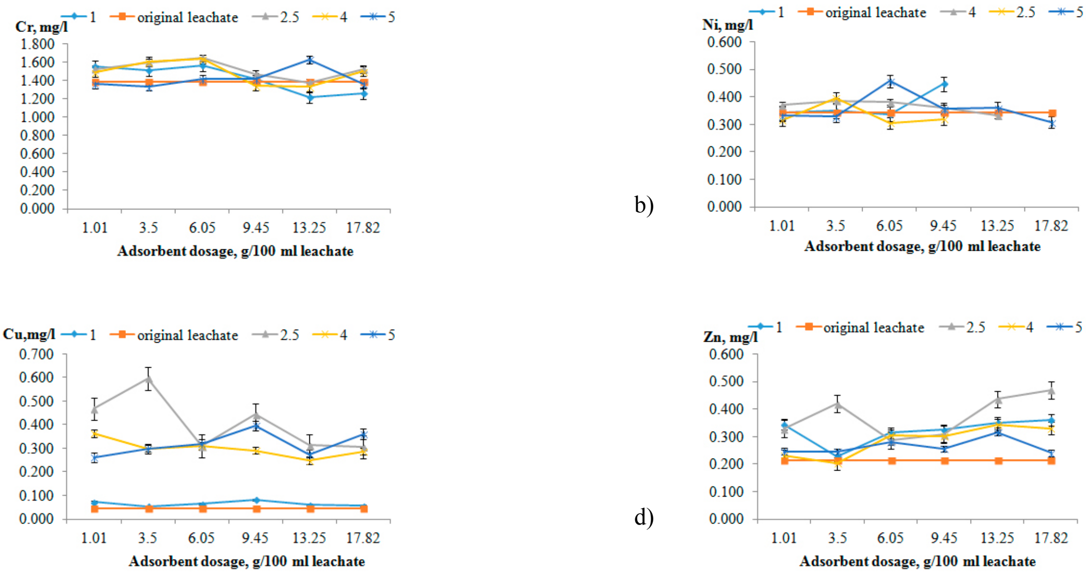


Fig. 3. Effect of biochar of different dosage on BOD_5 in landfill leachate. Values are mean ± SD

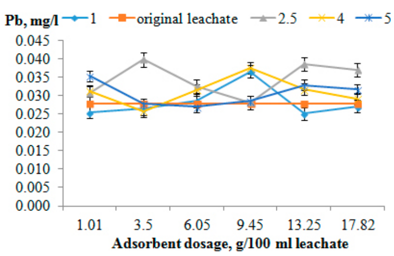
The optimal biochar dosage was 6.05 g/100 ml of landfill leachate. It was found that smaller particle size (1 mm) of the biochar promotes higher decrease in BOD_5 (in two times lower in comparison to untreated landfill leachate) due to the bigger contact surface of smaller particles with landfill leachate. Similar values were observed when BOD was decreased by 32.77% from landfill leachate by microbial fuel cells (Ganesh, Jambeck 2013).

Effect of biochar on PTEs concentration in leachate

The aim of experiment was to investigate the effect of woody biochar on the adsorption of Cu, Zn, Cr, Pb, Ni from landfill leachate. According to the Lithuanian law about wastewater Nr. D1–236 from 17 May 2006, requirements to the maximum allowable concentration (MAC) of PTEs in the landfill leachate to the wastewater treatment plant are the following: Zn – 3 mg/l, Ni – 0.5 mg/l, Cr – 2 mg/l, Pb – 0.5 mg/l, Cu – 2 mg/l. The results on PTE concentration on landfill leachate before and after treatment are presented in Fig. 4.



a) b) c) d)



e)

Fig. 4. Effect of biochar of different dosage and particle size on PTEs concentration in landfill leachate: a) Cr, b) Ni, c) Cu, d) Zn, e) Pb. Values are mean ± SD

After biochar treatment, content of Cr slightly decreased at dosage higher than 13.25 mg/100 ml of leachate and particle size 1 mm (Fig. 4a). The same tendency was observed for Pb at dosage higher than 13.25 mg/100 ml of leachate and particle size 1 mm (Fig. 4e).

While determination of concentration of Ni (Fig. 4b), the values for particle size of 1, 2.5 mm and dosage exceeding 9.45 mg/100 ml were below detection limit. Ni decreased with particle size 5 mm and dosage exceeding 13.25 mg/100 ml. No positive effect of biochar was observed for Zn (Fig. 4d) and Cu (Fig. 4c).

Nevertheless, treated landfill leachate met the requirements the wastewater treatment plant: Zn – 3 mg/l, Ni – 0.5 mg/l, Cr – 2 mg/l, Pb – 0.5 mg/l, Cu – 2 mg/l. Another option of landfill leachate treatment, as biological treatment reduced concentration of Ni in 15 times, Cr in 2, Cu in 1.1, but change in Zn and Pb was not noticeable (Petraitis 2009). Dairy manure biochar was more effective than lignocellulosic rice husk biochar in adsorption of Pb, Cu, Zn from multi-metal solutions (Tan *et al.* 2015).

Conclusions

1. After treatment by Scots pine biochar, pH of landfill leachate slightly increased: smaller particle size (1 and 2.5 mm) increased pH of landfill leachate more than biochar of bigger particle size; bigger dosage of biochar favored increase in pH. Moreover, pH of the biochar increased after the contact with landfill lachate from 7.52 to 9 at the particle size of 5 mm.
2. Optimal parameters for decreasing of BOD_5 were particle size 1 mm and dosage 6.05 g/100 ml of leachate. It was found that smaller particle size (1 mm) of the biochar promotes decrease in BOD_5 in two times lower in comparison to untreated landfill leachate.
3. Cr and Pb decreased at particle size 1 mm and dosage higher than 13.25 mg/100 ml of leachate. Ni decreased at particle size 5 mm and dosage higher than 13.25 mg/100 ml of leachate.
4. Biochar treatment provided no positive effect on Zn and Cu retention in landfill leachate. Nevertheless, treated landfill leachate met the requirements for Cu, Zn, Ni, Pb, Cr of the wastewater treatment plant.

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PAGAMINTA IŠ PUŠIES BIOANGLIS, SKIRTA CU, ZN, CR, PB, NI ADSORBUOTI IR BDS_5 MAŽINTI SĄVARTYNO FILTRATE

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Santrauka

Sąvartyno filtratas yra labai toksiška ir pavojinga nuotekų rūšis dėl sudėtingų komponentų, tokių kaip amoniakas, metalai ir organiniai junginiai, savybių. Sąvartynų tvarkymo technologijos, pvz.: flotacija, koaguliacija / flokuliacija, nusodinimas, oksidacija, mikro-, ultra-, nanofiltracija, atvirkštinis osmosas, yra brangios, nes jų užtikrinimas reikalauja terpės regeneravimo. Taip pat galimas antrinių atliekų susidarymas, kuris sukelia atliekų šalinimo problemą. Šiame darbe buvo ištirtas Zn, Ni, Cr, Pb ir Cu šalinimas iš Kazokiškių sąvartyno filtrato. Kazokiškių sąvartynas yra pagrindinė Vilniaus rajono komunalinių atliekų šalinimo vieta. Sąvartyno operatorius yra suinteresuotas alternatyviais pirminio sąvartyno filtrato valymo būdais, siekiant sumažinti atvirkštinio osmoso būdo naudojimą dėl brangaus technologinio proceso. Vienas iš siūlomų pirminio sąvartyno filtrato valymo būdų – adsorbcija naudojant bioanglį. Dėl specifinio paviršiaus ploto, gerai išvystytos porėtos struktūros ir paviršiaus funkcionalumo bioanglis yra naudojama kaip pigus adsorbentas, skirtas adsorbuoti PTE iš vandeninių tirpalų. Bioanglis buvo pagaminta iš šakninės pušies (*Pinus sylvestris L.*) medžio masyvo (po išdrožimo) pirolizės būdu, esant didžiausiai degimo temperatūrai 700 °C. Degimo procesas vyko 45 minučių, deguonies trūkumo sąlygomis. Laboratorinė analizė parodė, kad PTE, tokios kaip Zn, Ni, Cr, Pb, Cu, buvo sąvartyno filtrate prieš jam patenkant į vandens valymo įrenginius. Taigi, tyrimo tikslas buvo įvertinti PTE (Zn, Ni, Cr, Pb, Cu) valymo efektyvumą adsorbcijos būdu naudojant bioanglį, pagamintą iš pušies. Ištirti veiksniai, darantys įtaką adsorbcijos efektyvumui, tokie kaip bioanglies dalelių dydis (1, 2,5, 4, 5 mm) ir bioanglies dozė (1,01, 3,5, 6,05, 9,45, 13,25, 17,82 g / 100 ml filtrato). Taip pat buvo analizuojamas bioanglies poveikis sąvartyno filtrato pH, BDS_5, PTE adsorbcijai. Rezultatai parodė, kad optimalūs parametrai BDS_5 sumažinti ir Cr bei Pb sulaikyti buvo bioanglies dalelių dydis 1 mm ir dozė 6,05 g / 100 ml filtrato bei 1 mm ir daugiau kaip 13,25 g / 100 ml filtrato atitinkamai. Teigiamas poveikis Cu ir Zn nebuvo užfiksuotas.

Reikšminiai žodžiai: medienos bioanglis, adsorbcija, metalai, sąvartyno filtratas, BDS5.