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2019

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Book of proceedings - 5th International Conference
WASTES: Solutions, Treatments and Opportunities

EDITION
CVR - Centro para a Valorização de Resíduos

EDITORS
Fernando Castro, Cândida Vilarinho,
Joana Carvalho

COVER DESIGN
Rui Ferreira

ISSN
2183-0568

september 2019

HEAVY METALS REMOVAL OF LEACHATES FROM A MECHANICAL BIOLOGICAL MUNICIPAL SOLID WASTE TREATMENT PLANT FOR USE AS FERTILIZERS

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ABSTRACT
Leachates produced from treatment plants contains carbon, nitrogen, phosphorus, potassium and trace elements. This work aims to develop heavy metals removal processes using solid adsorbents synthetized at CIMO and LSRE-LCM laboratories at Polytechnic Institute of Bragança, such as activated carbon produced from a compost material from the same treatment plant and modified clays obtained through a partnership with a Kazakhstan institution, to adequate the leachate from the composting line of a mechanical and biological treatment facility, into commercial fertilizers which fit the requirements of the European Legislation. Preliminary results show that the adsoption materials promoted a reduction in the heavy metals content, but this reduction also affected the organic carbon content. However, the activated carbons presented a better potencial for heavy metals removal.

Keywords: Heavy metals removal, adsorption process, leachate treatment, fertilizers.

INTRODUCTION
Leachate is a waste product, which means that no direct production costs are associated, instead it implies expensive treatment processes to be discarded. The use of leachates in agriculture also means that the costs at waste treatment plants can be reduced. However, due to the nature of the leachates, they may contain heavy metals, phytotoxic substances such as ammonia, organic compounds of low molecular weight and high salt content [1], [2]. The content of organic carbon, nutrients and contaminants depends on the nature of the raw material, the conversion processes applied, the operational conditions [3], [4]. The characteristics of landfill leachate differ by many factors such as the composition of waste, elapsed time of the landfill, geochemical properties of the site and climate of the region. Municipal landfill leachates typically contain high ammonium and organic concentration [5]–[7].

The aim of this work is the testing of heavy metals removal processes using solid adsorbents synthetized at CIMO and LSRE-LCM laboratories at Polytechnic Institute of Bragança such as activated carbon produced from the compost residue generated in the same treatment plant and modified clays obtained from a partnership with a Kazakhstan institution, to adequate a leachate from the composting line of a mechanical and biological treatment facility, into commercial fertilizers which fit the requirements of the European Legislation.

MATERIALS AND METHODS

The samples were obtained from the leachate storage tank from a composting line of a mechanical and biological treatment plant of organic wastes at the company Resíduos do Nordeste, EIM (Mirandela, Portugal). The samples were collected in February 2019, and then were stored at 4°C in 5 L PET bottles. The samples were centrifugated, filtered and the supernatant was taken to analysis. The adsorbent materials were active carbon produced from the compost material generated in the treatment plant and acid activated clays obtained in a partnership with a Kazakhstan institution.
The activated carbon is produced from the compost provided by Resíduos do Nordeste, which is washed with distilled water, dried for 12h at 110°C, powdered and sifted, for homogenization. Different amounts of the compost were mixed with 30 mL of distilled water to obtain different initial concentrations and heated to targeted temperature as presented in Table 1. Then, the solids were separated by vacuum filtration (pore size 0.45 µm), washed and dried for 15h at 100°C.

Table 1. Composition and treatments used in the active carbon produced from the compost.

Sample	Reaction time (h)	Compost mass (g)	Reaction temperature (°C)
AC 10	4	3.00908	230
AC 11	2	3.00037	230
AC 12	2	2.00591	150

The natural clays, obtained from 4 diferent locations at Kazakhstan named ASA, KAA, AKA and KOA, were purified with a mixture of sodium acetate and acetic acid. Acid activated clays samples were prepared by adding 3 g of the natural clay into a 250 mL three necked round bottom flask, and 150 mL of 4 M solution of H_2SO_4. The resulting suspenion was stirred at 80 °C during 3 h. The supernatant was discharged and the activated clay was repeatedly washed until neutral pH. The activated clay was recovered and then dried in air static oven at 60 °C overnight.
10mL of the leachate for the active carbon and 20mL for the clays are mixed with 0.1g or 0.2g of each one of the solid adsorbents samples for 48 hours at room temperature, centrifugated at 9000rpm and the supernatant is reserved at 4ºC. The samples were characterized using TOC analysis, performed with 1:500 dilution, in a Shimadzu TOC-L equipment. Heavy metals quantification was performed by digesting the samples with HNO_3/HCl during 48 h at 60°C, then filtrated using a 0.45 µm syringe filter in a 50 mL volumetric flask, completed with a 5% HNO_3 solution, and afterwards analysed by atomic absorption spectroscopy using a Varian SpectrAA 220 apparatus.

RESULTS AND DISCUSSION

Total Organic Carbon (TOC) and heavy metals content of original and filtered leachates are summarized in Table 2 for samples collected in February 2019 from the compost leachate storage facility.

Table 2. Total Organic Carbon (TOC) and heavy metals content of original leachates and adsorbed leachates.

Samples	**%TOC**	**Zn (mg/kg)**	**Cu (mg/kg)**	**Cd (mg/kg)**	**Pb (mg/kg)**	**Ni (mg/kg)**	**Cr (mg/kg)**
EU 2016	3	1500	600	3	120	50	2
Original	2.81	468.6	101.6	0.37	4.76	116.33	10.74
Original Filtered	2.79	252.78	241.15	0.91	4.11	148.93	9.83
AC 10-0.1	2.03	505.55	263.07	0.81	4.11	11.71	6.67
AC 11-0.1	1.98	252.78	21.92	1.31	1.03	128.85	6.32
AC 12-0.1	2.02	252.78	241.15	1.01	1.03	125.5	6.67
AC 10-0.2	2.30	505.55	284.99	0.60	1.03	147.26	6.32
AC 11-0.2	2.36	252.78	306.91	1.01	1.03	3.35	7.37
AC 12-0.2	2.07	252.78	21.92	0.50	1.03	95.38	8.43

ASA 0.1	2.48	252.78	197.3	0.70	4.11	61.91	8.43
KAA 0.1	2.39	1011.10	131.53	0.81	1.03	18.41	13.70
AKA 0.1	2.39	1263.88	197.30	0.60	2.06	170.68	10.18
KOA 0.1	2.37	758.33	438.45	0.30	2.06	199.13	13.35
ASA 0.2	2.41	1263.88	372.68	1.51	1.03	103.75	9.83
KAA 0.2	2.51	1263.88	43.84	1.31	5.14	63.59	11.24
AKA 0.2	2.38	758.33	438.45	0.70	1.03	162.32	11.59
KOA 0.2	2.52	1011.1	87.69	0.70	6.17	87.01	12.99

The original leachate obtained at February 2019 presents a organic carbon content lower than the requirements of the EU fertilizers legislation (3% of TOC) for liquid organo-mineral fertilizers
The adsorption processes were tested using the filtered leachate samples removing the effect of the suspended solids and to ensure better separation after the adsorption process. Each treated leachate sample was identified by the adsorption solid used, as presented in Table 2.
The adsorption materials showed interactions with the organic carbon present in the leachate, which promoted visible removal of this carbon material from the liquid phase. The activated carbon promoted greater TOC removal in comparison with the active clays, which could affect the heavy metals removal since it is possible that the organic carbon would occupy the adsorption centers blocking the suppression of heavy metals. The adsorption materials showed interaction with the heavy metals present in the leachates, although it is notorious that the leachate heterogeneity affects greatly the results. Nevertheless Zn, Cu, Cd and Pb contents always fullfil the requirements. On the other hand, Ni and Cr still present higher content than the minimum allowed in the legislation. The samples treated with activated carbons produced from compost show lower heavy metals content.

CONCLUSION

The concentrated leachate cannot be used, at this point, as a fertilizer because it does not fit all the legislation requirements, but it still displays potential for future use. It shows high TOC contents. Although the adsorption materials promoted a reduction in the heavy metals content, this reduction also affected the organic carbon content, which is not an intented effect since it can affect negatively the fulfillment of the TOC requirements. Overall the activated carbons produced from the compost presented a better potencial for heavy metals removal. Nevertheless ion-exchage resins will be now tested for a more efficient heavy metals removal in order to minimize possible secondary elimination of usefull components such as nutrients or organic carbon.

ACKNOWLEDGMENTS

This work was financially supported by: Project VALORCOMP, funded by FEDER through Programme INTERREG V-A Spain – Portugal (POCTEP) 2014–2020 and Associate Laboratory LSRE-LCM - UID/EQU/50020/2019 - funded by national funds through FCT/MCTES (PIDDAC).

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