ECOTOXICOLOGICAL EVALUATION WITH EISENIA FETIDA GROUPS IN RELATION TO THE DEVELOPMENT OF LDPE MATRIX COMPOSITES TO MOTIGATE THE IMPACTS GENERATED BY DRAINAGE ACID MINERAL

Marcelo Gryczak*, Janine Wong, Christina Thiemann, Benoit Ferrari, Cesar Liberato Petzhold
* Universidade Federal do Rio Grande do Sul, marcelo.gryczak@ufrgs.br

RESUMO
A extração de carvão mineral, além do desenvolvimento econômico, gera riscos e passivos ambientais em barragens. Durante o processamento, 60% do total extraído são resíduos que causam vários impactos ambientais, como instabilidade geotécnica devido à inclinação ou erosão, geração de ácido e liberação de metais no solo. Por outro lado, o consumo de polímeros do tipo PEBD é outra preocupação ambiental devido ao alto consumo e baixa degradação no meio ambiente. O artigo dedica-se a avaliar a mitigação dos impactos ambientais produzidos por resíduos de mineração de carvão através da elaboração de compósito polimérico de PEBD reciclado com 0, 20, 40, 60, 80% em peso, reforçado com resíduos de mineração utilizando grupos de *Eisenia fetida* para avaliação dos parâmetros ecotoxicologicos do sistema solo. Os resultados mostram que a incorporação de resíduos polimericos de PEBD nos compósitos evita a drenagem ácida e também diminui os vestígios de íons metálicos no lixiviado e seu potencial de contaminação no solo. Alguns materiais podem ser usados para mitigar os riscos ambientais, fixando substâncias potencialmente nocivas ao meio ambiente em sua estrutura interna.

PALAVRAS-CHAVE: Ecotoxicologia, resíduo de mineração de carvão, PEBD, *Eisenia fetida*.

ABSTRACT
Extraction of mineral coal, in addition to economic development, generates environmental risks and liabilities in dams. During processing, 60% of the total extracted are wastes that cause various environmental impacts, such as geotechnical instability due to slope or erosion, acid generation and release of metals in the soil. On the other hand, the consumption of LDPE-type polymers is another environmental concern due to the high consumption and low degradation in the environment. The article aims to evaluate the mitigation of environmental impacts produced by coal mining waste through the preparation of recycled LDPE polymer composite with 0, 20, 40, 60, 80% by weight, reinforced with mining residues using groups of *Eisenia fetida* to evaluate the ecotoxicological parameters of the soil system. The results show that the incorporation of polymeric residues of LDPE in the composites avoids acid drainage and also reduces the trace of metallic ions in the leachate and its potential contamination in the soil. Some materials can be used to mitigate environmental risks by fixing substances potentially harmful to the environment in their internal structure.

KEY WORDS: Ecotoxicology, coal-mining waste, LDPE, *Eisenia fetida*.

INTRODUCTION

Mineral coal is an important source of energy and in order to overcome operational problems and environmental issues with its use, currently the researches are focused on higher yield and quality of coal, as well as on mitigating and overcoming environmental problems related to its production process (Ward, 2016).
About 45% of all electricity generated in the world is related to the use of thermal power plants, using traditional energy resources such as coal, peat, fuel oil, among others (Chen; Xu, 2010).
Brazilian coal production in 2014 was about 13 million tons, with the following participation: Rio Grande do Sul (54.9%), Santa Catarina (43.7%) and Paraná (1.4%) and a total turnover of R$: 1,209.12 billion (Mineral, 2016).
The problems related to coal-mining waste become critical due to the fact that they generally contain concentrations of metals and sulfur (Shao, et al. 2010).
After beneficiation procedures, approximately 65% of coal extracted from underground mines is discarded in waste deposits. On average, sulfur content in this coal waste is about 6%, most of it in the pyritic form (S-FeS_2), corresponding to 12% pyrite by mass (Gomes; Mendes; Costa, 2011).
The main cause of acid drainage formation is the oxidation of sulfide minerals, such as FeS_2 pyrite. Acid drainage results from the exposure of these minerals to oxygen, water and microorganisms (Johnson; Hallberg, 2005).
Therefore, there is a need to reduce the impacts related to the coal-mining waste, this can occur enabling the reuse of this residual material (Zhengfu, et al. 2010) according to the reviews performed, the recovery and reuse of these wastes

is one of the alternatives in the final disposal of these materials. Due to its composition, coal-mining waste can be used efficiently as raw material in the formulation of materials in construction (Taha, et al. 2017).
Polymers have played a vital role in the materials industry. Polymers consumption worldwide is growing at an annual rate of 5%, with a total annual consumption of over 300 million tonnes (Orzolek, 2017).
Polyethylene is a highly application thermoplastic polymeric material being marketed in different shapes and colors. Low density polyethylene (LDPE) has a branched chain structure, which decreases the degree of crystallinity and density, also decreases the resistance because it reduces the intermolecular bonding forces (Ramesh; Palanikumar; Reddy; Hemachandra, 2017).
The properties of the polymers have motivated its use in numerous products and applications. However, such proliferation entails an environmental hazard if not treated correctly at the end of its useful life (Lastra-Gonzales, 2016).
One of the main problems in the production and consumption of these materials, is the environmental impact of the plastic waste accumulated in the environment or in landfills, due to its longevity in the natural environment to be degraded (Sanchez, et al. 2017). The life cycles of the polymeric materials through their recycling can transform them into products through conversion processes, such as injection molding or extrusion (Ragaert; Delva; Van Geen, 2017).
Innovations that reduce the environmental impact generated by production and consumption activities are generally considered essential in the transition of more sustainable economies and societies and help mitigate the traditional dichotomy between competitiveness and sustainability (Bocken, et al. 2014).
The world market for sustainable building materials is expected to grow by $ 116 billion in 2013 to $ 254 billion by 2020 (Choudhury, 2016).
Thus, to achieve the objective of the sustainable development in the materials industry, the selection of raw materials plays a key role. There is ongoing research into the viability of raw materials from reusable waste as alternative materials. Currently the research is related to the use of municipal solid waste, agricultural waste and industrial waste (Raut; Gomez, 2017).
The remarkable increase in waste production requires the development of sustainable procedures to maximize the recovery of the beneficial properties of these materials. Studies have shown that bioassays can be used successfully to detect the risks of residual materials and other compounds (Vasickova, et al. 2016)
Therefore, ecotoxicology is established as an environmental monitoring tool because it is based mainly on the response of these organisms to chemical stressors. In order to study the phenomena of intoxication and with the purpose of preventing, interrupting or remedying this process within the system in which the substance is being evaluated (Azevedo; Chasin, 2014).

OBJETIVES

The article is dedicated to evaluate the mitigation of the environmental impacts produced by coal-mining waste through the elaboration of a recycled LDPE polymer composite with 0, 20, 40, 60, 80% by weight, reinforced with coal-mining waste using ecotoxicological tests in soil as parameters.

METHODS

The coal-mining waste was acquired at a mining company located in the city of Treviso in the state of Santa Catarina / Brazil.
The preparation of the raw materials consisted of drying and milling the coal-mining waste with obtaining grains smaller than 0,05 mm and in the sorting of the LDPE residue, where they were also dried and crushed.
The composites were made through the homogenizing of the raw materials in a dynamic thermomixer. The equipment used was Thermo Scientific ™ HAAKE ™ Rheomix.
The matrix / reinforcement fractions used in the composites formulation were from 20% to 80% by weight, with 20% intervals, resulting in four different composites formulations and the 0 and 100% reinforcement controls, the composites materials were processed at 110°C for 10 minutes at a speed of 50 rpm.
To obtain the leachate, the samples of the composite material were milled, sifted and used with particle size between 2.0 and 6.3 mm.
In relation to the production of the mineral acid drainage through the the leached extract, the samples were submitted to the standard test method for laboratory weathering of solid materials using wet cell, described in D5744 (ASTM, 2018).

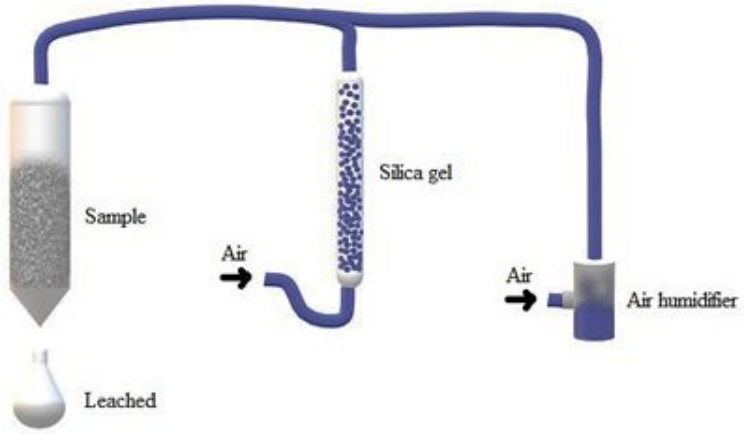

Figure 1: Leachate production system. Source: Author of Work.

The acid leachate was used to humidify the soil test as an ecotoxicological characterization system, with aqueous holding capacity of 60% in systems soil, in the test of aquatic system the leachate was used directly as an aqueous medium.
The elemental characterization of the coal-mining waste was performed by x-ray fluorescence. The chemical characterization of the leachate samples consisted in the quantification of the inorganic ions sulfide and sulfate by ion chromatography and the analysis of iron and aluminum by atomic absorption.
The avoidance behavior tests were performed according to 17512-1 (ISO, 2008), which specify the rapid scanning method in assessing the bioavailability of contaminants in soils and their influence on behavior in a group of *Eisenia fetida* individuals. The behavior related to food activity was performed according to 18311 (ISO, 2015), which defines the method for testing the effects in soil contaminants on the food activity through bait-lamina, using *Eisenia fetida* bioindicator group.

RESULTS

The results of the elemental chemical characterization by x-ray fluorescence of the coal-mining waste shows the predominance of iron, sulfuric and aluminum oxides, totaling 75% of the composition of the coal-mining waste. These compounds are intimately bound to the pyrous material commonly found in coal-mining waste.
The pH results of the leachate samples demonstrate a higher acidification of the systems related to increase the fraction of coal-mining waste in the composites materials formulation.

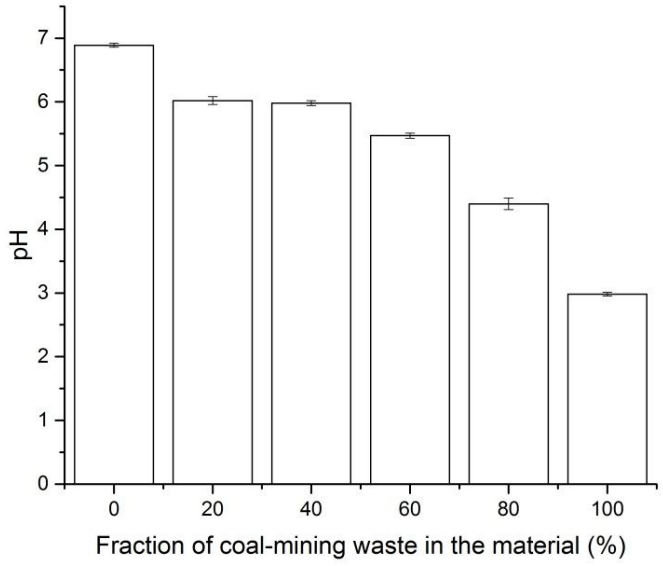

Figure 2: Leachate pH results. Source: Author of Work.

The leachate sample of the coal-mining waste obtained pH 2.98, with the formulation of the composites material of 40% polymer matrix the pH of the leachate was around 5.40 a decrease of 55% in the acidification of the system in relation to the sample of coal-mining waste. Studies have shown that the oxidation of pyrite in leach cells containing coal-mining waste can generate acidity for at least 5 years (Weiler; Amaral Filho; Schneider, 2016). The iron, aluminum and sulfate contents in the leachate samples, are presented in the subsequent.

Table 1: Results of chemical characterization of leachate samples. Source: Author of Work.

Samples	Iron content (mg/L)	Aluminum content (mg/L)	Sulfate (mg/L)
Negative control	< detection limit	< detection limit	< detection limit
20% CMW	0.41	< detection limit	237,0
40% CMW	2.43	< detection limit	245,0
60% CMW	9.79	< detection limit	301,0
80% CMW	9.19	< detection limit	893,0
100% CMW	34.99	10.53	1245,0

Note: % CMW is percentage of Coal-mining waste in the formulation of composites.

The results of iron content show the decrease of the traces dragged by the leachate, since the sample with only 20% of polymeric matrix obtained a decrease of 380% in the release of iron in the leachate.
The behavioral results of avoidance in two sections, demonstrate that the control soil performs an attractive function for the groups evaluated in relation to the test soil in the leachate sample with a fraction of 100% of the coal-mining waste.

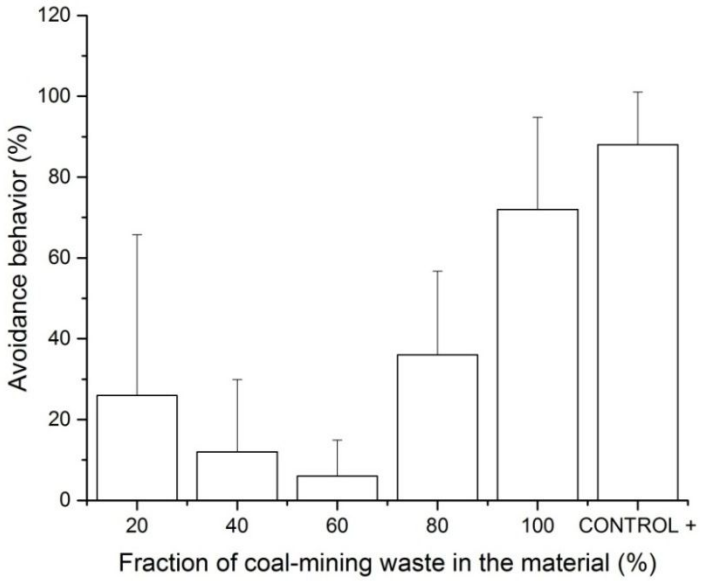

Figure 2: Avoidance behavior results. Source: Author of Work.

The results of the samples with 100% of coal-mining waste showed avoidance behavior of about 94% in the worms groups analyzed, indicating impact on the behavior of earthworms related to intrinsic habitat limitation in the analyzed sample. Thus, the leakage rates exceeded the maximum limit established by the standard that is >80%, in which this threshold characterizes the system as toxic potential. Earthworms can expose themselves and absorb contaminants from the soil solution by direct contact (Vijver, et al. 2013).
In the case of the samples of leachate from the formulated composite materials, the results were below the limit of >80%, the presence of the fractions of the polymer matrix within the composite system seems to stimulate the reduction of traces of contaminants in the leachate and, consequently, the reduction of contaminants solubilized in the soil. However, the other samples of the composite materials showed non-linear concentration-response results,

however within the limits parameters established by the standard. This greatly simplifies behavioral analysis because activity changes are rarely linear (Gauthier; Vijayan, 2018).
The results of the feed activity rates of the *Eisenia fetida* groups, demonstrate the relation of the presence of the polymer matrix within the formulation of the composite material and the interference in the formation of the leachate in these materials.

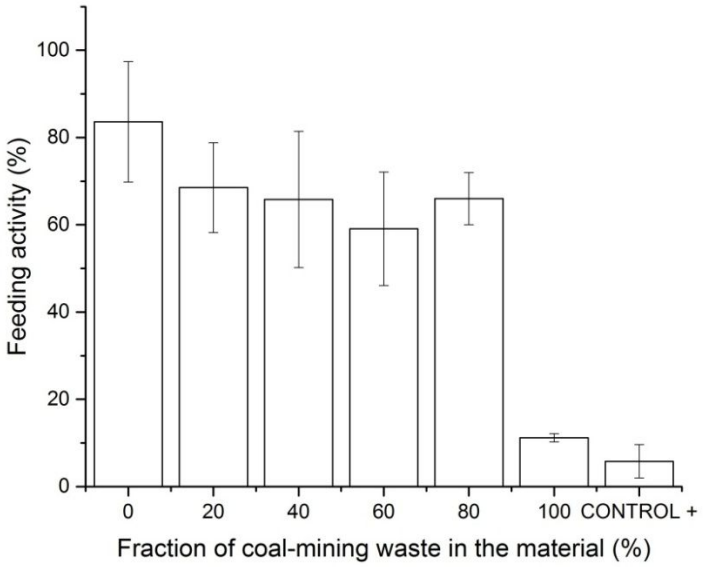

Figure 3: Feeding activity results. Source: Author of Work.

Thus, the sample of leached with 100% coal-mining waste obtained a food activity rate of approximately 10%. This characteristic can be understood as a strategy of natural survival, avoiding the ingestion of toxins. This strategy is commonly used in earthworms to avoid poisoning (Shi, et al. 2017).
Studies have shown that certain concentrations of metals may have adverse effects on fauna activity in soils and subsequently on the ability of organic matter to decompose (Lahr; Kools; Van Der Hout; Faber, 2008).
Since the sample with a fraction of only 20% recycled polymer matrix within the composite system obtained a feed activity rate higher than 60%, these results are within the standard deviation of the samples with 0% of the mineral coal fraction, demonstrating the efficiency in the use of a hydrophobic matrix within the formulation and the blocking in the traces of contaminants in the production of the leachate.

CONCLUSIONS

The results show that coal-mining waste present's characteristics of chronic contamination in relation to the evaluated ecotoxicological parameters in soil and that the formulation of a composite material of polymeric matrix tends to block the formation of acid drainage, traces of toxic elements in the leachate and its potential of contamination. Some materials can be used to mitigate ecotoxicological risks by fixing potentially harmful substances to the environment in their internal structure (Kobeticova; Černy, 2017).
The wettability of the polymer at the time it is being fused with the coal-mining waste entails encapsulating the contaminants within the matrix.

BIBLIOGRAPHIC REFERENCES

1. ASTM. D5744. **Standard test method for laboratory weathering of solid materials using a humidity cell. American Society for Testing Materials.** 2018.
2. Azevedo, F. A.; Chasin, A. A. M. **As bases toxicológicas da ecotoxicologia.** São Carlos: RIMa. p. 340. 2004.
3. Bocken, N. M. P. et al. A literature and practice review to develop sustainable business model archetypes. **Journal of cleaner production**, v. 65, p. 42-56, 2014.
4. Chen, W.; Xu, R. Clean coal technology development in China. **Energy policy**, v. 38, n. 5, p. 2123-2130, 2010.
5. Choudhury, I.A. Renewable and Sustainable Materials, **In Reference Module in Materials Science and Materials Engineering**, Elsevier, 2016.

6. Gauthier, P. T.; Vijayan, M. M. Nonlinear mixed-modelling discriminates the effect of chemicals and their mixtures on zebrafish behavior. **Scientific reports**, 8, 2018.
7. Gomes, C. J. B., Mendes, C. A. B., Costa, J. F. C. L. The environmental impact of coal mining: a case study in Brazil's Sangão watershed. **Mine Water and the Environment**, *30*(3), 159-168. 2011.
8. ISO, 17512-1. **Soil quality – Avoidance test for determining the quality of soils and effects of chemicals on behaviour – Part 1: Test with earthworms (*Eisenia fetida and Eisenia andrei*).** 2008
9. ISO, 18311. **Soil quality — Method for testing effects of soil contaminants on the feeding activity of soil dwelling organisms — Bait-lamina test**, 2015.
10. Johnson, D. B. ; Hallberg, K. B. Acid mine drainage remediation options: a review. **Science of the total environment,** v. 338, n. 1, p. 3 -14, 2005.
11. Kobeticova, K.; Černy, R. Ecotoxicology of building materials: a critical review of recent studies. **Journal of Cleaner Production**, vol. 165, p. 500-508. 2017.
12. Lahr, J.; Kools, S.A.E.; Van Der Hout, A.; Faber, J.H. Combined effects of zinc and earthorms density on soil ecosystem functioning. **Soil Biology and Biochemistry**. 40, 334-341, 2008.
13. Lastra-Gonzales, P. et al. Comparative analysis of the performance of asphalt concretes modified by dry way with polymeric waste. **Construction and Building Materials**, v. 112, p. 1133-1140, 2016.
14. Mineral, DNPM. Ministry of Mines and Energy of Brazil. **National Department of Mineral Production** (DNPM), 2016.
15. Orzolek, M. **A Guide to the Manufacture, Performance, and Potential of Plastics in Agriculture**. Elsevier, 2017.
16. Ragaert, K.; Delva, L.; Van Geen, K. Mechanical and chemical recycling of solid plastic waste. **Waste Management**, 2017.
17. Ramesh, M.; Palanikumar, K.; Reddy, K. Hemachandra. Plant fibre based bio-composites: Sustainable and renewable green materials. **Renewable and Sustainable Energy Reviews**, v. 79, p. 558-584, 2017.
18. Raut, A. N.; Gomez, C. P. Development of thermally efficient fibre-based eco-friendly brick reusing locally available waste materials. **Construction and Building Materials**, v. 133, p. 275-284, 2017.
19. Sanchez, F. A. et al. Polymer recycling in an open-source additive manufacturing context: Mechanical issues. **Additive Manufacturing**, v. 17, p. 87-105, 2017.
20. Shao, Y. et al. Ash deposition during co-firing biomass and coal in a fluidized-bed combustor. **Energy & Fuels**, v. 24, n. 9, p. 4681-4688, 2010.
21. Shi, Y. et al. Comparative effects of lindane and deltamethrin on mortality, growth, and cellulase activity in earthworms (*Eisenia fetida*). **Pesticide biochemistry and physiology**, v. 89, n. 1, p. 31-38, 2007.
22. Taha, Y. et al. Coal mine wastes recycling for coal recovery and eco-friendly bricks production. **Minerals Engineering**, v. 107, p. 123-138, 2017.
23. Vasickova, J. et al. Ecotoxicity of arsenic contaminated sludge after mixing with soils and addition into composting and vermicomposting processes. **Journal of hazardous materials**. vol. 317, p. 585-592. 2016.
24. Vijver, M. G. et al. Oral sealing using glue: a new method to distinguish between intestinal and dermal uptake of metals in earthworms. **Soil Biology and Biochemistry**, v. 35, n. 1, p. 125-132, 2003.
25. Ward, C. R. Analysis, origin and significance of mineral matter in coal: an updated review. **International Journal of Coal Geology**, v. 165, p. 1-27, 2016.
26. Weiler, J., Amaral Filho, J. R. D., Schneider, I. A. H. Coal waste processing to reduce costs related to acid mine drainage treatment-case study in the Carboniferous District of Santa Catarina State. **Engenharia Sanitaria e Ambiental**, 21(2), 337-345. 2016.
27. Zhengfu, B. I. A. N. et al. Environmental issues from coal mining and their solutions. **Mining Science and Technology (China)**, v. 20, n. 2, p. 215-223, 2010.