ECOTOXICOLOGICAL EVALUATION IN AQUATIC SYSTEMS IN RELATION TO THE DEVELOPMENT OF LDPE MATRIX COMPOSITES TO MITIGATE THE IMPACTS GENERATED BY DRAINAGE ACID MINERAL

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ABSTRACT
Extraction of mineral coal, in addition to economic development, generates environmental risks and liabilities. During processing, 60% of the total extracted are wastes that cause various environmental impacts, such as acid generation and release of metals into aquatic systems. 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 Vibrio fischeri for evaluation of the ecotoxicological parameters of the aquatic 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 of contamination in the aquatic system. Some materials can be used to mitigate environmental hazards by fixing substances potentially harmful to the environment in their internal structure.

KEY WORDS: Ecotoxicology, coal-mining waste, LDPE, Vibrio Fischeri.

INTRODUCTION
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). Coal is still one of the main sources of fossil energy used for centuries to boost the economy of several countries. However, the coal mining activity is criticized for the environmental impact and especially for the large amount of waste generated during mining (Fan; Zhang; Wang, 2014). 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-FeS₂), 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 FeS₂: 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).

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).

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).

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 using *Vibrio fischeri* bioindicator in aquatic systems 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 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).
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 evaluation of inhibition of bioluminescence in bacteria was carried out according to 11348 (ISO, 2007), which defines the guidelines for determining the inhibitory effect of aqueous samples on light emission using *Vibrio fischeri* bioindicator.

**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.
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>
<thead>
<tr>
<th></th>
<th>Iron content (mg/L)</th>
<th>Aluminum content (mg/L)</th>
<th>Sulfate (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative control</td>
<td>&lt; detection limit</td>
<td>&lt; detection limit</td>
<td>&lt; detection limit</td>
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<tr>
<td>20% CMW</td>
<td>0.41</td>
<td>&lt; detection limit</td>
<td>237.0</td>
</tr>
<tr>
<td>40% CMW</td>
<td>2.43</td>
<td>&lt; detection limit</td>
<td>245.0</td>
</tr>
<tr>
<td>60% CMW</td>
<td>9.79</td>
<td>&lt; detection limit</td>
<td>301.0</td>
</tr>
<tr>
<td>80% CMW</td>
<td>9.19</td>
<td>&lt; detection limit</td>
<td>893.0</td>
</tr>
<tr>
<td>100% CMW</td>
<td>34.99</td>
<td>10.53</td>
<td>1245.0</td>
</tr>
</tbody>
</table>

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.

The results of bioluminescence inhibition using *Vibrio fischeri* bioindicators, demonstrated the efficiency of the formulation of composite materials with recycled polymer matrix in inhibiting the bioluminescence caused by the leachate of the coal-mining waste.

The underlying principle is the correlation of changes in the kinetic attributes of the bioluminescent reaction with the toxicity of the test substance (Dunn; Bethany; Rader; Markel, 2015).

According to the results the samples of leached with 100% coal residue obtained an inhibition rate of about 70%, compared to the composite systems formulated with recycled polymer matrix fractions that obtained bioluminescence inhibition rates lower than 20%, emphasizing the blocking of traces of contaminants from the mineral coal residue.
present in the leachate. Acid drainage can cause extensive contamination of surface water and groundwater, with relevant levels of toxicity, pH change and dissolved metal concentration (SIMATE, NDLOVU, 2014).

CONCLUSIONS

The results show that coal-mining waste present’s elements with possibility contamination in relation to the evaluated ecotoxicological parameters in aquatic systems 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, by the wettability of the polymer at the time it is being fused with the coal-mining waste entails encapsulating the contaminants within the matrix.

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