

VALORIZATION OF LEACHED WATERS THROUGH CONVERSION IN LIQUID FERTILIZERS

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Dissertation presented to the School of Agriculture of the Polytechnic Institute of Bragança, to obtain the Master's degree in Environmental Technology in the scope of the Double Diploma agreement with the Federal Technological University of Paraná.

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July, 2019

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Acknowledgments

To God for being present in all moments of my life.

My mother Jacira and my father Valdir for the unconditional support they show for my dreams, for the love and encouragement they have always given me.

My sisters Kely and Fernanda, for all affection, dedication and understanding during this time of my absence.

To my nephews for giving me strength to continue when it seemed impossible.

To my supervisor Professor Paulo Brito, for the opportunity to participate in this project, for all guidance and freedom offered. To my co-supervisors Professor Juliana Bortoli Mees and Professor Helder Gomes, for the confidence.

To the Polytechnic Institute of Bragança and the Federal Technological University of Paraná for the opportunity to carry out this work, under the double diploma agreement.

To my laboratory advisor Jonathan Cardoso, for all knowledge passed on, guidance, patience and availability.

To Jordan Sena Campos, for all support, encouragement and affection.

To my Master's friends (Francieli, Felipe, Lucas, Murilo, Rafael, Juliana, Ighor, Paulo and Jessica) who became a family, thank you for the friendship, we were a point of mutual support.

My soul sisters Thamiris Tavolone and Evelyn Ferraz, for making themselves present even from a distance.

This work was carried out under the scope of Project VALORCOMP, funded by FEDER through Programme INTERREG V-A Spain – Portugal (POCTEP) 2014–2020.

Finally, to all who have somehow been part of this period and collaborated to carry out this work, I will be eternally grateful.



Abstract

An unprecedented demographic explosion occurred in the last decades at a global level. The negative impacts of this event stand out, affecting the social, economic and mainly environmental spheres. In the environmental aspect, an important consequence is the growing production of solid wastes, due partially to the population increase. However, the development of effective technologies for the treatment of these wastes did not accompany such growth, and currently the most used method for this is landfill disposal. Even with the possibility of alternatives, the use of landfills for the disposal of solid wastes will be necessary over a long period, with the inevitable consequence of the generation of leachate streams.

The objective of this work is the development, design and implementation of processes for physicochemical conversion of leachate liquid effluents from a composting process in liquid fertilizers with a standardized and reproducible composition.

The leachate sample was collected in February 2019 from the slurry storage tank of the company “Resíduos do Nordeste”, EIM (Urjais, Mirandela, Portugal). The stream is produced and recovered from a composting line from a mechanical and biological waste treatment plant. From this original sample, three additional materials were obtained: a filtered sample for the removal of the solid fraction (Filtro 03/04), two concentrated samples by simple distillation, with two concentration levels in volume basis: 1,19× and 1,85× in relation to the original leachate sample.

The four samples (the original leachate and the three processed samples) were submitted to a sequence of analyzes, in order to compare its composition and properties with the current Portuguese and European legislation specifications for liquid fertilizers. The selected characterization parameters were: Total Organic Carbon (TOC), pH, Conductivity, Percentage of Dry Matter, Density, and Heavy Metals, Phosphorus, Potassium and Nitrogen contents.

Adsorption tests were performed with the Filter 03/04 sample, with two adsorbents of different origin, the first produced from an organic compound, resulting from a centralized composting process, obtained from the same landfill that provided the

Original sample. The second adsorbent tested is activated clays, originating from four different deposits in Kazakhstan.

After treatment with the adsorbents, the same analyzes were performed previously, aiming to evaluate the efficiency of the adsorbents.

The characterization results were then used to verify the framework for later use of the original leachate and/or the processed samples as liquid organomineral fertilizers, and to assess the specific needs of composition tuning for the non-processed leachate sample. A concentration process for the original sample of 1,19× (v/v) has been determined to allow the reaching of at least 3% TOC, a content legally required. Additionally, treatment is required for the removal of nickel and chromium from the samples. The metals zinc, copper, cadmium and lead have been quantified and are within the limits specified in the Regulation of the European Parliament and of the Council (2019).

A flowchart for the proper treatment of this leachate was proposed, with the intention of using it as liquid organomineral fertilizer.

Keywords: *Leachate; Organic Fertilizer; Organomineral Fertilizer; Wastewater treatment.*

Resumo

Uma explosão demográfica sem precedentes ocorreu nas últimas décadas a nível global. Destacam-se os impactos negativos deste evento, afetando as esferas social, econômica e principalmente ambiental. No aspeto ambiental, uma consequência importante é a crescente produção de resíduos sólidos, em parte devido ao aumento populacional. No entanto, o desenvolvimento de tecnologias eficazes para o tratamento desses resíduos não acompanhou esse crescimento, e atualmente o método mais utilizado para isso é o descarte em aterros sanitários. Mesmo com a possibilidade de alternativas, o uso de aterros sanitários para a disposição de resíduos sólidos será necessário por um longo período, com a inevitável consequência da geração de caudais de chorume.

O objetivo deste trabalho é o desenvolvimento, proposta e implementação de processos de conversão físico-química de efluentes líquidos lixiviados, de um processo de compostagem, em fertilizantes líquidos com uma composição padronizada e reprodutível.

A amostra de lixiviados foi coletada em fevereiro de 2019 a partir do tanque de armazenamento de chorume da empresa “Resíduos do Nordeste”, EIM (Urjais, Mirandela, Portugal). O fluxo é produzido e recuperado de uma linha de compostagem de uma estação de tratamento de resíduos mecânica e biológica. Desta amostra original, três materiais adicionais foram obtidos: uma amostra filtrada para a remoção da fração sólida (Filtro 03/04), duas amostras concentradas por destilação simples, com dois níveis de concentração em base volumétrica: 1,19× e 1,85× em relação a amostra original.

As quatro amostras (o lixiviado original e as três amostras processadas) foram submetidas a uma sequência de análises, de modo a comparar a sua composição e propriedades com as atuais especificações da legislação portuguesa e europeia para fertilizantes líquidos. Os parâmetros de caracterização selecionados foram: teor de carbono orgânico total (TOC), pH, condutividade elétrica, percentagem de matéria seca, densidade e metais pesados, fósforo, potássio e nitrogênio.

Foram realizados testes de adsorção com a amostra Filtro 03/04, com dois adsorventes de origem diferente, o primeiro produzido a partir de um composto

orgânico, resultante de um processo de compostagem centralizada, obtido do mesmo aterro sanitário que forneceu a amostra Original. O segundo adsorvente testado, são as argilas ativadas, originárias de quatro depósitos diferentes do Cazaquistão.

Após o tratamento com os adsorventes foram realizadas as mesmas análises feitas anteriormente, com o objetivo de avaliar a eficiência dos adsorventes.

Os resultados da caracterização foram então utilizados para verificar a estrutura para posterior utilização do lixiviado original e/ou as amostras processadas como fertilizantes organominerais líquidos, e para avaliar as necessidades específicas de ajuste da composição. Um processo de concentração para a amostra original de 1,19× (v/v) foi determinado para permitir o alcance de pelo menos 3% de TOC, um conteúdo legalmente requerido no Regulamento do Parlamento Europeu e do Conselho (2019). Além disso, é necessário um tratamento para a remoção de níquel e cromo das amostras. Os metais zinco, cobre, cádmio e chumbo foram quantificados e estão dentro dos limites especificados no Regulamento do Parlamento Europeu e do Conselho (2019).

Um fluxograma para o tratamento adequado desse lixiviado foi proposto, com o intuito de utilizá-lo como fertilizante organomineral líquido.

Palavras-Chave: *Lixiviado; Fertilizante Orgânico; Fertilizante Organomineral; Tratamento de Efluentes.*

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ACRONYMS AND ABBREVIATIONS

ACP- Activated Carbon Powder

AGC- Activated Granular Carbon

AOP- Advanced Oxidation Processes

As- Arsenic

BOD- Biochemical Oxygen Demand

Cd- Cadmium

COD- Chemical Oxygen Demand

C_{org}- Organic Carbon

Cr- Chromium

Cu- Copper

Hg- Mercury

IC- Inorganic Carbon

IPB- Polytechnic Institute of Bragança

K- Potassium

LD- Detection limit

LQ- Quantification limit

N- Nitrogen

Ni- Nickel

N_{org}- Organic Nitrogen

P- Phosphorus

Pb- Lead

TC- Total Carbon

TFS- Total Fixed Solids

TKN- Total Kjeldahl Nitrogen

TOC- Total Organic Carbon

TS- Total Solids

TVS- Total Volatile Solids

USW- Urban Solid Waste

Zn- Zinc

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1. Introduction

We are witnessing an unprecedented demographic explosion. The negative impacts of this event stand out, affecting the social, economic and mainly environmental spheres.

In the environmental aspect, the growing production of solid waste is highlighted, due to the population increase. However, the quality for the treatment of these residues did not accompany such growth, and currently the most used method for this is the sanitary landfill, being possible still the incineration with energy recovery, selective collection (recycling) and organic valorization.

Even with other options, the use of landfills for the final destination of solid waste will be necessary for a long time, with an inevitable consequence, the generation of leachate streams.

The leachates represent the main source of pollution of these infrastructures. It can be defined as a set of liquids arising from the organic matter decomposition process, from the moisture present in the materials deposited in the pile, from natural water sources (infiltration) and from the microbial activity (Sá *et al.*, 2012).

It is not possible to create a faithful characterization of percolated liquids because of their inconstancy, the variability in the composition of the leachate is influenced by the age and characteristics of the residues and the type of technology used in landfills.

According to Kjeldsen *et al.* (2010), the pollutants in urban solid waste leachate are divided into four main groups: dissolved organic matter (TOC), inorganic macrocomponents, heavy metals and organic xenobiotics. Nevertheless, other elements can be found as: barium, lithium, mercury, arsenic, cobalt, among others.

As previously mentioned, solid wastes have water in their constitution, however, the greater part comes from the percolation, originating from the precipitation. During the decomposition of the solid residues, the water dissolves numerous chemical elements, among them, some heavy metals, that become the leachate.

These leaching liquids must be drained to treatment cells attached to the landfill. The lack or inadequate treatment of this type of effluent can cause surface water pollution, which would lead to deoxygenation of the water, and ammoniacal toxicity, causing damage to benthic flora and fauna (Russo, 2005).

Even so, the biggest negative impact that a landfill can cause is groundwater pollution. Thus, an adequate waterproofing, drainage and treatment system of this effluent is therefore necessary.

Normally, after the treatment of percolated liquid, the treated effluent is released into streams. However, other options are emerging for the leachate appreciation. An alternative would be its use for the fertilization of soils, being this the focus of study of this work. However, due to the variability in leachate composition, the treatment for this purpose becomes a relevant challenge.

1.1. Objective

The objective of this work is the development, design and implementation of processes for the physical-chemical conversion of leachate liquid streams from a composting process, into liquid fertilizer materials, with standardized and reproducible composition.

1.2. Structure of the work

The paper is divided into 8 chapters, which begins with the Introduction chapter, which is based on a bibliographical review, presenting the interest of the theme, focusing on the possible impacts on the environment. The second chapter was devoted to the state of the art, which introduces the most common methods of treatment and the clarification of the theme. The legal framework is found in chapter three, presenting the conditions and limits established in current legislation. In the fourth chapter, the methodology used is presented, the sample features are described, and information is given about the analysis performed, equipment used, experimental procedures used, and the tests performed with two adsorbents of different origin. In the fifth chapter, Results and Discussion, the presentation, treatment and discussion of the data obtained for the analyzed samples and for the tests with the adsorbents are made. In the sixth chapter, a procedure is proposed for the treatment of leachate, with the purpose of using it as fertilizer. The seventh chapter presents the general conclusions, establishing a relation with the objectives proposed in the work. Finally, chapter eight, contains suggestions for future work, linked to this project.

2. State of the Art

2.1. Solid urban waste: a problem of societies

Society changed its way of interacting with waste during different epochs of human history, among them we can cite: The Industrial Revolution, which brought the increase of productivity and, consequently, the population growth concentrated in some regions; the rise of international trade, especially after the Second World War and the increasing and constant changes of technologies. These are historical milestones that have led to an increase in the amount of urban solid waste per capita (Pinho, 2011).

Pinho (2011) informs that these misbehaviors are responsible for the change in the way society started to consume and discard products. Consumerism, often unbridled, has become a major contributor to increased waste generation, as it is no longer used only for material survival, reflecting on other stages of the product's life cycle.

Final destination waste is the most important step for this study, considering that treatments are needed to reduce the environmental, social and economic impacts of this product at the end of its useful life.

Mankind has developed several techniques in order to mitigate these impacts, among them we can mention the treatments in landfill, the composting of organic residues and the incineration.

2.2. Composting as a waste treatment and disposal structure

The purpose of waste treatment is to change the characteristics, which can occur by physical, chemical, biological or mixed routes, in a way that reduces the volume and the degree of harmfulness. Treatment and destination are considered as the most important phases of the waste system, because in these steps, if the correct measures are not taken, environmental problems can arise.

The most commonly used technologies for waste recovery are: landfill deposition, incineration and composting.

Sousa (1996) says that the higher the rate of reuse and recovery of solid waste, the lower the amounts to be deposited, extending the useful life of the landfill and reducing the cost of exploration.

The search for alternatives has become necessary due to the increasing generation of waste that needs to be destined and the lack of available area, besides being a form of environmental care. Composting is widely used to decrease the volume to be deposited in the soil, these reductions are of the order of 40% (Sousa, 1996).

Composting can be defined as the process of biological decomposition of organic matter under controlled aerobic conditions of temperature and humidity, generating a stable product (De Bertoldi *et al.*, 1983), which we call organic fertilizer.

For Mota *et al.* (2009), composting is the process of biological treatment of the organic portion of the residues, allowing a reduction of the volume of the residues and the transformation of these into a compound to be used in agriculture as a soil reconditioning, that is, this material is incorporated into soils cultivated as fertilizer for plants.

The urban solid waste (USW) has different composition of household residues and services (public cleaning, industries), so USW can have different decomposition times for organic compound generation (Siqueira & Assad, 2015).

There are three major types of composting. Domestic, agricultural and centralized composting. Centralized composting occurs in facilities where waste from a given region is routed and treated. Centralized composting can be done in open systems (batteries) or in closed systems (reactors).

The benefits of composting can be categorized as follows: utilization of waste from the region; partnership with private companies and public institutions; development of clean technologies for the use of waste; solution for the supply of organic fertilizer; soil recovery; not dependence on synthetic inputs; decrease in the cost of production; correct destination for environmental liabilities; compliance with environmental legislation; participatory management; among others (Mota *et al.*, 2009).

Although it is one of the best destinations for organic waste, composting also has a few disadvantages, the main one being the generation of leachate, a liquid effluent

resulting from the process of degradation of the pile that needs treatment before being discarded.

2.3. Formation of leachate

Reis (2005) says that the formation of leachate in composting systems operated in uncovered areas occurs in a similar way and is influenced by the same factors as percolates generated in landfills.

El-Fadel *et al.* (2002) states that the leachate is generated by leaching, discontinuous and non-uniform, resulting in the removal of soluble organic and inorganic compounds that are incorporated in the liquid.

The leachate has a high contamination potential, due to the organic load and physicochemical composition. The physical-chemical portion is variable and is dependent on factors such as: local pluviometric conditions and the time of decomposition of the compounds. Due to the degradation of substances such as fats and carbohydrates, percolate contains high concentrations of heavy metals and suspended solids (Silva L. M., 2009).

Law Decree n° 152/2002 states in its Annex II, item 2.2 (b), that the leachate treatment units must be dimensioned in order to deal with the entire leachate flow rate associated with the exceptional rainfall conditions of the site. The drainage and treatment systems of the leachate should be designed considering the high organic load and the variation of the flow rates, which depend on the atmospheric precipitation.

In regions such as the north of Portugal, the different seasons of the year must be considered, where there are low flow rates in the summer and high flows in the winter.

2.4. Environmental impacts resulting from USW treatment

The undue final destination of USW has become a problem of modern society, especially regarding the harm caused to the environment, such as pollution of air, soil and water (Mota *et al.*, 2009).

According to Mota *et al.* (2009), the decomposition of USW with or without the presence of oxygen in the medium tends to cause the generation of natural gases in the mass. This release of gases becomes the source of risk of gas migration, explosions or even respiratory diseases if there is direct contact. In the soil, the negative impacts occur through the physical-chemical alterations thereof, which makes the environment conducive to the development of disease transmitters, besides the possibility of contamination of the soil by percolated liquid, compromising it. In the water, this type of pollution changes the characteristics of the aquatic environment, due to the leachate generated in the USW decomposition process, associated with the rainwater and possible sources of pollution around the source of contamination.

The contamination of the leachate in the soil and its dispersion in the water can occur not only while the landfill is in operation, but also after its deactivation, since the organic substances continue to degrade. Areas close to landfills have high levels of organic compounds and heavy metals. Populations living in the vicinity of these sites also have elevated levels of these compounds in the blood. Thus, these solid waste deposits are potential sources of exposure to populations. There are reports of high risks for some cancers, congenital anomalies, abortions, and neonatal deaths in these populations and in populations close to them (Gouveia, 2012).

2.4.1. Leachate

The most striking characteristics of the leaching liquids are the high concentrations of organic matter and heavy metals, which imply a particularly complex treatment process. The generation of leachates is unique in each treatment unit and is dependent on factors such as inputs: precipitation water, moisture from the USW deposited in the pile, water from the aerator material; and outputs: surface runoff waters, evapotranspiration, evaporation and water consumed by the biological process (Russo, 2005).

The amount of leachate generated also varies with the seasonality, since the humidity can vary according to the season of the year and the operational state of the composting cell.

2.4.2. Treatment of leachate

2.4.2.1. Qualitative characteristics of leachate

The leachates from composting systems have variable characteristics, as mentioned previously.

Ripley *et al.* (1984) conducted a study of the evolution and characteristics of leachates in 16 different sanitary landfills, such as electrical conductivity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, soluble solids, hardness, alkalinity, heavy metals, chlorides e sulfates, pollutants considered essential for legislative procedures. The data did not present evolutionary behavior over time, even with the different lifetimes of landfills.

An analogous study was conducted by Ehrig *et al.* (1989), 15 landfills in Germany were studied for 5 years. The results showed that parameters such as BOD, COD and heavy metals underwent changes with the evolution of the process of decomposition of urban solid waste, more precisely from the anaerobic acid phase to the methanogenic phase. COD presented high variability in the first years of the study, with a relative stabilization at the end.

In the United Kingdom, Robinson *et al.* (1985) conducted a study with detailed information on landfill leachates that, like the work done by Ehrig *et al.* (1993) in Germany, presented reduction of the concentrations of some parameters with the arrival of the methanogenic phase in the process of decomposition of urban solid waste. In this study, the establishment of this phase occurred at the end of three years of operation of half of the landfills evaluated. In one of the landfills, the methanogenic phase had not yet been reached after eight years of operation.

The N, P, K and Na macronutrients present higher concentrations in the acidic phase than in the methanogenic phase of the waste degradation process (Ehrig, 1989).

The concentrations of heavy metals in leachates are similar in urban wastewater and thus depend on the characteristics of the waste and the operation mode of composting cells or landfills. The highest values are found in the acid phase, due to the redox potential and the pH variation (Russo, 2005).

Russo (2005) reports that the chemical composition of the percolates varies with the age of degradation and the stage of the biogas generation phase. In the acid phase, high values are found for BOD, COD, total organic carbon (TOC), heavy metals and nutrients, whereas in the methanogenic phase, the BOD, COD and TOC have lower values. To determine the leachate treatment process as a function of COD, the author suggests that if the percolate has COD above 10,000 mg/L, BOD/COD ratio between 0,4 and 0,8, low ammoniacal nitrogen and significant concentration of volatile fatty acids, the treatment can be performed anaerobically or aerobically.

The treatment for compost cell leachates will be different for each plant, due to the variability of the characteristics of the urban solid waste in degradation and the age of the composting system analyzed, being able to undergo changes in the treatment system during the useful life of the cell.

Due to so many individual particularities for each treatment process, a detailed study and characterization of the parameters of the leachate to be treated is necessary.

Some treatment possibilities will be presented in the next topic.

2.4.2.2. Precipitation, Coagulation and Flocculation

Several techniques can be used to remove metals from solutions, making effluents suitable for disposal into watercourses. Techniques such as chemical precipitation, coagulation-flocculation, flotation, ion exchange, adsorption, membrane filtration, liquid-liquid extraction are among the most investigated.

The main advantages of chemical precipitation are that the technology and alkalizing agents are available and when the objective is only to treat the effluent, the operation and maintenance of the equipment is considered relatively simple. This process consists in increasing pH, leaving the medium under conditions of low solubility for the metal hydroxides, which precipitate in the form of hydroxides or various complexes. Thus, colloidal solids are formed, which require coagulation/flocculation steps to separate from the liquid phase (Neto *et al.*, 2008).

According to Russo (2005) the colloidal particles have dimensions ranging from 1 nm to 1 μ m and are characterized by a large specific surface and therefore are very

sensitive to surface forces. In order to facilitate the gravitational removal of the colloidal particles, during the coagulation process, these particles are destabilized to form larger particles, and for that to occur, coagulants are used. The most commonly used coagulants are aluminum and iron salts. These salts have an acidic behavior and its efficiency depends on the alkalinity of percolates.

The incorporation of flocculating agents takes place to facilitate the agglomeration of the colloidal particles. The most used flocculants are activated silica and clay (inorganic), and polyacetates (organic). Sometimes aluminum and iron can also be used, which can behave as flocculants, since their low solubility allows them to precipitate (Russo, 2005).

The precipitation process is applied to the removal of heavy metals, causing the formation of metal hydroxides or sulfides (Neto *et al.*, 2008).

Russo (2005) found a greater efficiency in the use of this method in more advanced percolates (low BOD/COD), or when the leachate had a previous biological treatment. In contrast, a new leachate, which has a high concentration of small volatile fatty acids, tends to precipitate less, so the removal involves only a smaller fraction of the organic components of the leachate and less efficiency.

Ehrig (1989) presented a study in which efficiency of COD removal in leachate with low BOD (<25 mg/L) was obtained in the order of 50%, obtaining a low BOD/COD ratio. The agents used were iron and aluminum salts, and both presented the same results.

2.4.2.3. Chemical Oxidation

Chemical oxidation is the process in which electrons are removed from a substance by increasing its oxidation state. In most cases, the oxidation of organic compounds, while being thermodynamically favorable, exhibits slow kinetics. Some oxidative processes have the great advantage of not generating solid by-products (sludge) which does not promote phase transfer of the pollutant (as adsorption in active carbon, for example). The final products are carbon dioxide (CO₂) and water (H₂O). As examples of oxidizing agents, hydrogen peroxide (H₂O₂) and ozone (O₃) can be mentioned. When the oxidizing agent is chlorine (Cl₂) or its derivatives (e.g. hypochlorite), great care

must be taken when the effluent presents high levels of organic matter, since it is possible to have organochlorine compounds as byproducts, which, in some cases, have carcinogenic, teratogenic and mutagenic properties. Permanganate is another oxidizing agent widely used in the oxidation of pollutants (Graciano *et al.*, 2012).

The advanced chemical oxidation processes (AOP) are efficient technologies for destroying organic compounds that are difficult to break down and sometimes present in low concentrations. Since there is no formation of toxic byproducts, they are often considered as clean technologies. Chemical oxidation consists of oxidizing complex organic compounds to simple molecules (Castro, 2014).

In general, the great disadvantage of oxidative processes is the high cost. However, these processes have been used in the treatment of old landfill leachates since they have low biodegradability and high concentration of recalcitrant compounds.

2.4.2.4. Membrane Separation Processes

Costa (2015) says that membrane filtration exploits the semipermeable properties of some membranes in order to cause separation between the solvent (water) and the pollutants present in the leaching waters. The separation is achieved by the passage of the leachate under pressure through semipermeable membranes.

The membrane separation processes basically involve four categories: reverse osmosis, nanofiltration, ultrafiltration and microfiltration. It can be said that what differentiates the categories of separation by membranes are the pore diameters and the type of intensity of the driving force applied to carry out the separation of the contaminants. (Galvão & Gomes, 2015).

What differs membrane separation processes from the conventional filtration process is that the flow of water is parallel to the membranes, i.e., not every percolate to be treated needs to pass through the membrane, the small particulate solids and the organic and inorganic compounds are separated, and further, the pressure in the operating system of the membrane separation systems is greater than in the conventional filtration processes (Russo, 2005).

This system has been applied to the treatment of leachate. The landfill at Vennenberg-Lingen, Germany, has a treatment system consisting of activated sludge oxidation tanks with ammonia removal and a section of two reverse osmosis modules, which showed good results. It was observed that the efficiency of the process increased with the existence of a biological pretreatment (Weber & Holz, 2012).

Weber (2012) emphasizes the disadvantages of the membrane technique due to the high concentration of organic components and the precipitation of inorganic components, which can cause problems of fouling and bioaccumulation on the surface of the membrane. High energy consumption is another negative point, besides the limitations concerning low productivity related to the need of low treated flows.

2.4.2.5. Adsorption

The phenomenon of adsorption involves the accumulation of substances on a surface or an interface (Weber & Holz, 2012). The interfaces may be related to the liquid-liquid, gas-solid, gas-liquid, or liquid-solid phases, the latter being of interest in wastewater treatment.

According to Campos (2011), the use of activated granular carbon (AGC) or powder (ACP) has been commonly used in the treatment of landfill leachates to remove biodegradable compounds due to their characteristics of having large surface area, high adsorption capacity and microporous structure.

The adsorption process occurs through the transfer of compounds present in the liquid phase to the reactive surface, the matter adheres to the "voids" of the activated carbon due to physical and/or chemical interactions (Campos, 2011).

The adsorption application of carbon dioxide can be used to remove 50-70% of COD and N-NH_4^+ , and its applicability, especially in the reduction of refractory (non-biodegradable) organic compounds, is suggested by Wiszniowski *et al.* (2006).

Li *et al.* (2010) conducted experiments with stabilized leachate by combining the use of coagulants (FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, PolyChloride and Ferric PolySulfate) with ACP. The tests were conducted, firstly, to obtain the optimal dosage of each coagulant and, later, with the addition of different dosages of ACP ranging from 0,5 to 50 g/L to the

supernatant. It was possible, therefore, to compare the combined action of each coagulant with the addition of ACP. The best results obtained by the researchers were with the addition of 10g ACP/L in 90 minutes of contact time, with a significant reduction of COD (53-70%), Suspended Solids (> 93%), Turbidity (> 99%) and Toxicity (78%).

Jimenez *et al.* (2004) says that since the recovery of metal ions from dilute solutions using classical methods is inefficient and, considering the current environmental policy, alternative methods have been investigated, such as electro dialysis, osmosis reverse polarization, ultrafiltration and adsorption in natural materials, which promote the selective and reversible retention of metal cations. Among the natural materials that can be used, zeolites have received attention due to their low cost and simplicity in the process. Its microporous structure allows the mobility of ions through the channels and cavities, providing selectivity to ion exchange processes.

2.4.2.6. Biological Treatment

The biological treatment processes that can be applied in the treatment of leaching water share the same principles of processes used in the treatment of urban waste water, taking advantage of the ability of bacteria to degrade organic matter into simpler compounds. Its application also aims at the removal of nutrients such as nitrogen and phosphorus.

In treatment plants that use biological processes, some parameters such as: temperature, pH and dissolved oxygen are controlled, in order to provide an environment that favors the growth of microorganisms, and increase the efficiency of biodegradation (Telles, 2010).

Telles (2010) carried out treatability tests in order to verify if the diversity of compounds present in the leachate could be assimilated by a bacterial community. The tests were carried out with leachate samples pretreated by the ozonation process with 0,06 g.L⁻¹ ozone for 15 minutes and 45 minutes of reaction; leachate samples pretreated by the removal process of ammoniacal nitrogen by entrainment with air followed by ozonation with 0,06 g.L⁻¹ ozone for 15 minutes and 45 minutes of reaction; leachate samples pretreated only by the process of removal of ammoniacal nitrogen by

entrainment with air; and crude leachate. The tests were conducted in six reactors and a previously acclimated biomass was used in the tests.

The performance of the treatability test was evaluated by calculating COD removal in the six reactors. It was verified that the efficiency of removal of organic matter, represented by the removal of COD, was in the range of 80 to 86%.

Table 1 presents the effluent treatment processes and their applicability for the removal of different pollutants.

Table 1. Processes of treatments described.

Treatment Process	Application
Biologic treatment	Removal of organic matter
Coagulation / flocculation	Removal of color and turbidity, suspended solids and heavy metals
Chemical oxidation	Removal of organic and inorganic matter
Membranes	Removal of organic and inorganic matter
Adsorption	Removal of organic and inorganic matter and heavy metals

2.5. Final Destination

2.5.1. Application to soil

The method of treatment of leachates in the soil is recommended by several authors with the argument that the natural bacterial activity of the soil, combined with the physical processes (filtration and evaporation) and physical-chemical (ion exchange and adsorption) promote the purification of leachates. Thus, sandy soils tend to eliminate organic matter and clay soils with their great cation exchange capacity, potentiate the elimination of heavy metals. Another advantage pointed out is the fertilizer character of the leachate (Robinson & Maris, 1985).

New solutions have been studied for the use of pre-treated leachate, one of them is its application as a liquid fertilizer, being considered organic fertilizers. Organic fertilizers are safer at the ecological level. Bacteria and fungi in the soil decompose the

organic matter of the fertilizer and release the nutrients progressively and according to the requirements of the soil.

Pinto *et al.* (2005) carried out an experiment aimed at the use of leachate from forage crops in substrate for fertilization of orchards (this type of leachate can be considered like that extracted from compost piles). The authors concluded that this use as fertilizer may be a viable alternative to these leachates.

For a percolate to be used as liquid fertilizer, a pretreatment process is necessary. In order to analyze its nutritive composition for later use in the soil, it is still necessary that this leachate fulfills the legal requirements to be considered liquid fertilizer.

Decree-Law n° 103/2015 provides recommendations for the process of sanitizing the fertilizer matter, resulting from the composting process. The composting units shall, for an appropriate period, subject the wastes to conditions of temperature and humidity capable of inactivating the pathogenic micro-organisms and weed seeds and propagating material, as follows:

Systems in which the biological treatment of waste is carried out entirely by composting: (a) in static aerated stack systems where the waste pile is not revolved and is covered with a layer of material used as a thermal insulator, if the composting mass is to be aerated by means of insufflation or suction, the entire mass of the waste must remain for at least two weeks at a temperature of at least 60 °C and a degree of humidity of more than 40%; (b) in heavier pile systems where composting is periodically revolved, with or without forced aeration, the waste must be subjected for at least four weeks to conditions of temperature and humidity exceeding 55 °C and 40% , respectively, by carrying out at least three revolutions.

3. Legal Framework

The regulation of the European Parliament and of the Council of May 2019 defines fertilizers as: substance, mixture, micro-organism or any other material applied or intended for application to plants or rhizosphere, fungi or their myosphere, or intended for to form the rhizosphere or the myosphere, on its own or mixed with other materials, in order to provide nutrients to the plants or mushrooms or to improve their nutritional efficiency.

This Regulation lays down the criteria according to which waste material as defined in Directive 2008/98/EC may be no longer waste if it is part of an EU fertilizer product. In such cases, the recovery operation in accordance with this Regulation shall take place before the material ceases to constitute waste and the material is deemed to comply with the conditions laid down in Article 6 of that Directive and, consequently, is not a waste as soon as the EU declaration of conformity has been established.

According to European Parliament and Council (2019), in an organic fertilizer the contaminants must not exceed the following concentrations (see Table 2).

Table 2. Limit values of contaminants in liquid organomineral fertilizers.

Contaminants	Concentrations (mg/kg dry matter)
Biuret (C ₂ H ₅ N ₃ O ₂)	12000
hexavalent chromium (Cr VI)	2
Mercury (Hg)	1
Nickel (Ni)	50
Lead (Pb)	120
Arsenic (As)	40
Copper (Cu)	600
Zinc (Zn)	1500

Cadmium: If an organomineral fertilizer has a total phosphorus (P) content of less than 5% expressed as phosphorus pentoxide (P₂O) in mass: 3 mg/kg dry matter, or if an organomineral fertilizer has a total phosphorus (P) content of 5% expressed as

phosphorus pentoxide (P₂O) in bulk (phosphorus fertilizer): 60 mg/kg of Phosphorus pentoxide.

The regulation further provides that pathogens must not be present in organic fertilizers in a concentration higher than the limits indicated in Table 3.

Table 3. Concentration of pathogens that should not be exceeded.

Microorganisms under test	sampling plans			Limit
	n	c	m	M
Salmonella spp.	5	0	0	absence in 25g or 25 mL
Escherichia coli or enterococos	5	5	0	1000 in 1g or 1 mL

Source. Regulation of the European Parliament and of the Council (2019).

n- number of test samples,

c- number of samples in which number of bacteria expressed in colony forming units (cfu) and between *m* and *M*,

m- The limited value of the number of expressive services in the cfu considered satisfactory,

M- maximum value of the number of bacteria expressed in cfu.

The European Parliament and Council Regulation (2019) also sets out the limit values for organic matter and nutrients required for the product to be considered as organic-mineral liquid fertilizer.

A liquid organic-mineral fertilizer will contain at least one of following declared primary nutrients: Nitrogen (N), Phosphorus pentoxide (P₂O₅) or Potassium oxide (K₂O).

When a liquid organomineral fertilizer contains only a declared primary nutrient, said nutrient will be present in the following minimum concentrations:

- ❖ 2% by mass of Total Nitrogen (N), with 0,5% by mass of an organomineral fertilizer liquid organic nitrogen (N_{org}).
- ❖ 2% by mass of total phosphorus pentoxide (P₂O₅), or
- ❖ 2% by mass of Potassium oxide (K₂O) total.

The organic carbon (C_{org}) will be present in a liquid organomineral fertilizer at a minimum of 3% by mass.

In order to meet the requirements that are fundamental to the sustainable use of fertilizers with organic components, Decree No. 103/2015 establishes quality criteria for materials produced from waste and organic biodegradable materials. It also establishes that the production of these fertilizer materials, in accordance with the provisions of the said decree, configures the application of the end of residue status to the production of compound constituting as a product.

The decree of Law nº 103/2015 defines organic fertilizer as: the fertilizer whose nutrients are, in their totality, of vegetal origin and, or, animal. It also defines organomineral fertilizer as the fertilizer obtained by mechanical mixing of mineral fertilizers and organic fertilizers.

The Decree-Law nº 103/2015, contains in its Annex I the types of non-harmonized fertilizer material, separated by groups. Table 4 presents group 2, *Organic Fertilizers*, and Table 5 summarizes group 3, *Organomineral Fertilizers*.

Table 4. Group 2 - Organic Fertilizers.

N°	Type designation	Information on the procurement process and the essential components	Minimal nutrient content (% by mass). Indications concerning the determination of nutrients. Other indications.	Other indications concerning the type designation	Nutrients whose content it is necessary to declare. Forms and solubilities of nutrients. Other criteria
1	2	3	4	5	6
1	Whipped organic fertilizer (N)	Fertilizer obtained entirely from products or by-products of animal or vegetable origin only with a declared nitrogen content.	N organic: 3%. Organic matter: 50%	Other usual trade names may be added.	Organic Nitrogen and Organic Matter.
2	Organic fertilizer NPK	Fertilizer obtained entirely from products or by-products of animal or vegetable origin with declared nitrogen, phosphorus and potassium	N organic: 2%. P ₂ O ₅ total: 2%. K ₂ O total: 2%. N+ P ₂ O ₅ + K ₂ O: 10%. Organic matter: 50%	Other usual trade names may be added.	Total nitrogen, Organic nitrogen, Phosphorus soluble in mineral acids (total), Total potassium and Organic matter
3	Organic fertilizer NP.....	Fertilizer obtained entirely from products or by-products of animal or vegetable origin with declared nitrogen and phosphorus content.	N organic: 2% P ₂ O ₅ total: 3%. N+ P ₂ O ₅ : 6%. Organic matter: 50%	Other usual trade names may be added.	Total nitrogen, Organic nitrogen, Phosphorus soluble in total mineral acids, Total potassium and Organic matter
4	Organic fertilizer NK....	Fertilizer obtained entirely from products or by-products of animal or vegetable origin with declared nitrogen and potassium.	N organic: 3%. K ₂ O total: 6%. N+ K ₂ O: 10%. Organic Matter: 50%.	Other usual trade names may be added.	Total Nitrogen, Organic Nitrogen, Total Potassium and Organic Matter.

Source. Decree Law n°103 (2015).

Table 5. Group 3- Organomineral Fertilizers.

Nº	Type designation	Information on the procurement process and the essential components	Minimal nutrient content (% by mass). Indications concerning the determination of nutrients. Other indications.	Other indications concerning the type designation	Nutrients whose content it is necessary to declare. Forms and solubilities of nutrients. Other criteria
1	Nitrogenated organomineral fertilizer (N)	Fertilizer obtained by mixing products or by-products of animal or vegetable origin with mineral fertilizers and having only declared nitrogen content.	N total: 5% N organic: 1%. Organic matter: 25%	Other usual trade names may be added.	For types 1 to 5: 1 - Total nitrogen. 2 - Organic nitrogen. 3 - Organic matter.
2	Organomineral Fertilizer NPK	Fertilizer obtained by mixing products or by-products of animal or vegetable origin with mineral fertilizers and having declared contents of nitrogen, phosphorus and potassium.	N total: 5% N organic: 12%. P ₂ O ₅ total: 3%. K ₂ O total: 3%. N+ P ₂ O ₅ + K ₂ O: 15%. Organic matter: 25%	Other usual trade names may be added.	4 - If one of the forms of nitrogen (nitric, ammoniacal, urea and cyanamide) is present with a content equal to or greater than 1%, it may be declared.
3	Organomineral Fertilizer NP	Fertilizer obtained by mixing products or by-products of animal or vegetable origin with mineral fertilizers and having declared contents of nitrogen and phosphorus.	N total: 3% N organic: 1% K ₂ O total: 5% N ₂ +K ₂ O: 10% Organic matter: 25%	Other usual trade names may be added.	For types 2 and 3: 5 - Total phosphorus. 6 - Phosphorus soluble in neutral ammonium citrate if its content is equal to or greater than 2% (P ₂ O ₅) and less than this value is the water-soluble phosphorus content.
4	Organomineral Fertilizer NK	Fertilizer obtained by mixing products or by-products of animal or vegetable origin with mineral fertilizers and having declared nitrogen and potassium contents.	N total: 3% N organic: 1% K ₂ O total: 5% N ₂ +K ₂ O: 10% Organic matter: 25%	Other usual trade names may be added.	7 - Phosphorus soluble in neutral ammonium citrate and water if the of phosphorus soluble in water is equal to or greater than 2% (P ₂ O ₅). In this case, the latter solubility will also be declared.
5	organomineral fertilizer NK Fluid	Solution or Suspension of a type 4 fertilizer.	N total: 3% N organic: 1% K ₂ O total: 3% N ₂ +K ₂ O: 8% Organic matter: 12%	pH, Other usual trade names may be added.	For types 2, 4 and 5: 8 - Total potassium. 9 - Potassium soluble in water.

Source. Decree Law n°103 (2015).

4. Methodology

The leachate sample was collected in the leachate storage tank (see Figure 1) of the company Resíduos do Nordeste, EIM (Urjais, Mirandela, Portugal). The flow is produced and recovered from a composting line of a mechanical and biological waste treatment plant.



Figure 1: Leachate storage tank.

The storage tank has no cover and is susceptible to rainfall and runoff, which can cause leachate dilution.

The sample was collected in February 2019 and stored at 4 °C in 5 L bottle of polyethylene terephthalate (see Figure 2).



Figure 2. Original Sample.

This sample was characterized through the measuring of selected parameters, like: Total Organic Carbon (TOC), pH, Conductivity, Percentage of Dry Matter, Density, Heavy Metals, Phosphorus and Nitrogen (TKN).

The collected sample was named as "Original sample", and from this sample, three different processes were applied.

The first process was the concentration of the original sample, obtaining two samples. The second process was performed by centrifuging and filtering the original sample. These processes were carried out in order to evaluate the influence of the solids on the analyzed parameters and the concentration was made to reach parameters required by the legislation.

The concentration of the samples (see Figure 3) was carried out by heating 100 mL of the original sample and boiling it until the concentration of 3% of organic carbon was attained, eliminating at least 7 mL of water. This process resulted in 84 mL of 1,19 times concentrated sample from the original in volume, which was named "1,19×". The same procedure was used to concentrate another sample: 200 mL was used and after the concentration 108 mL was obtained, i.e. 1,85 times the original in concentration. This sample was named "1,85×", so that a percentage of 5% of total organic carbon would be reached.

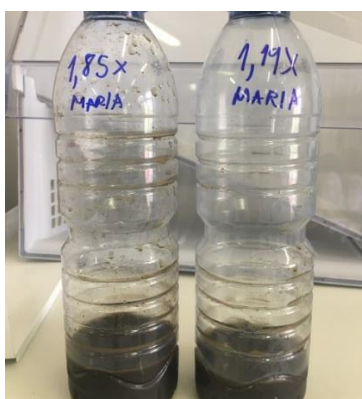


Figure 3. Concentrated samples.

For the preparation of the last sample, a centrifuge was used (see Figure 4) in order to facilitate the filtration of the solids contained in the original sample. 250 mL of the original sample was centrifuged, followed by vacuum filtration. Hence, 220 mL of sample without solids was obtained, which was named "Filtro 03/04" (see Figure 5).



Figure 4. Centrifuge.



Figure 5. Filtered sample.

4.1. Total Organic Carbon (TOC) analysis

TOC analyzes were performed on Shimadzu 5000A TOC-L equipment (Total Organic Carbon Analyzer). This apparatus operates by a catalytic combustion principle. This is achieved in a combustion pipe where the catalyst is contained, and heated to a temperature of 680 °C with a drag gas flow at 200 kPa. This gas must be synthetic air with a purity of 99,995%.

The analysis of TOC allows the estimation of the amount of organic matter present in the sample, where the organic carbon present is quantified.

The amount of organic carbon is given by the difference between Total Carbon (TC) and Inorganic Carbon (IC).

Total Organic Carbon (TOC) analysis was performed with a 1:500 dilution. 0,5 mL of sample was added to a 250 mL volumetric flask, and the volume of the flask was then quenched with distilled water. Measurements were performed in triplicate. Prior to the first measurement, the procedure was performed on the equipment using only

distilled water, in order to make sure that the equipment would not contaminate the sample. This step was repeated every time after the analysis of each sample, ensuring the nonexistence of possible contaminants which would affect the results.

The data acquired by the Shimadzu TOC-L equipment were then sent to the TOC-L Sample Table Editor program, where the values of TC, IC and consequently TOC were organized.

The same procedure for TOC analysis was applied for the four samples cited above.

4.2. Density

To obtain the density, the equipment of the brand *Anton Paar-Density meter-DMA-5000M* was used. The settings were adjusted so that the data was obtained at 20 °C.

20 mL of sample was put in a 50 mL beaker, and the equipment collected the sample through a capillary. This parameter was measured for all previously mentioned samples, and all analyzes were performed in triplicates.

To clean the equipment, a density measurement was made with ultrapure water before and after use.

4.3. pH and conductivity analyses

For the pH measurements, a WTW SenTix 41 pH electrode (see Figure 6) was used. For this measurement 90 mL of the leachate sample was added in a 100 mL beaker. Along with the effluent was added a magnetic bar and the beaker was placed on a magnetic heating plate. In this way the sample remained homogenized while being heated.

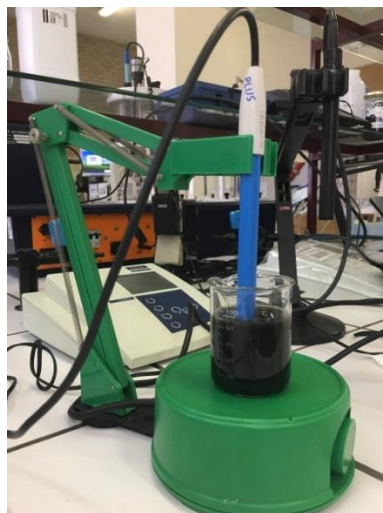


Figure 6. pH measurements.

The electrode for pH measurement was placed in the liquid sample when it was at 10 °C and again at 20 °C, thus measuring the respective pH values.

On the other hand, to assess the electrical conductivity of the sample, the WTW conductivity cell TetraCon 325 was used. In a procedure similar to the previous one, the electrical conductivity of the collected leachate was measured using the same beaker. The conductivity cell was inserted into the effluent on a magnetic heating plate, also at 10 °C and 20 °C.

This method was used for the analysis of pH and conductivity of the original sample, and 1,19×, 1,85× and Filtro 03/04 samples.

4.4. Dry matter

The total solids (ST) content, or dry matter, was determined by gravimetry after drying the material in an oven at 105 °C for 48 hours. The results were expressed in g per kg.

For the determination of this parameter, three empty crucibles were weighed and approximately 0,5g of sample was added in each one, weighing them again. The crucibles were brought to the oven at 105 °C for 48 hours and weighed after this period.

The dry matter determination was performed by the difference of the weighed values with the fresh and dry samples.

This analysis was performed in an analogous way for the original sample, and 1,19×, 1,85× and Filtro 03/04 samples.

4.5. Ash analysis

Ash analysis was determined after drying of the material at 450 °C. For the determination of this parameter, three empty crucibles were weighed and approximately 0,5g of sample was added in each one, weighing them again. The crucibles were brought to the muffle at 450 °C for 2 hours and weighed after this period were returned to the muffle for another hour and weighed again, this process was carried out until the weighed value became constant. Ash determination was performed by the difference of the weighed values with the fresh sample.

This analysis was performed in an analogous way for the original samples, 1,19×, 1,85× and Filtro 03/04.

4.6. Phosphorus

4.6.1. Preparation of standard solution and vanadomolybdc solution

- a) **Standard solution of 500 ppm (m/v) P₂O₅:** 0,9640 g of primary standard KH₂PO₄ in 99,5% purity, dried for 2 hours at 105 °C, was transferred to a 1000 mL volumetric flask, with distilled water. This solution contained 500 mg of P₂O₅ per liter (500 ppm, m/v).
- b) **Vanadomolybdc solution:** 20g of ammonium molybdate (NH₄MoO₄, p.a.) was dissolved in 200-250 mL of distilled water at 80-90 °C and allowed to cool. 1g of ammonium metavanadate (NH₄VO₃, p.a.) was dissolved in 120-140 mL of distilled water, after cooling the solution, 180 mL of concentrated nitric acid was added. Gradually the solutions of molybdate and

metavanadate were mixed. The solution was transferred to a 1000 mL volumetric flask, making up the volume with distilled water.

4.6.2. Preparation of the calibration curve

Pipette the standard solution 2,0 - 2,5 – 3,0 – 3,5 and 4,0 mL into 50 mL volumetric flasks, to each flask was added 20 mL of distilled water and 15 mL of the vanadomolybdic solution. The flasks were shaken and swollen with distilled water. These solutions contained 20, 25, 30, 35 and 40 ppm (m/v) of P_2O_5 , respectively.

The 5 flasks were allowed to rest for 10 minutes, so that color development was complete, the absorbance of the solutions at 400 nm was determined using the solution containing 20 ppm of P_2O_5 as blank.

4.6.3. Determination of Total Phosphorus Concentration

To determine the total phosphorus concentration, 10 mL of sample was used in a 250 mL beaker. Then 25 mL of concentrated nitric acid was added, allowing to boil gently for 45 minutes to oxidize the organic matter.

After this process, the beaker was allowed to cool and 10 mL of perchloric acid was added. This solution was carefully heated for one hour, replacing the acid if necessary, to prevent it from drying. After this period, the solution was let to cool and 50 mL of distilled water was added, continuing the heating for another 5 minutes.

After this process, the liquid was vacuum filtered with paper filter, and then transferred to a 100 mL volumetric flask, along with 15 mL of reagent (Vanadomolybdic solution) and diluted with distilled water. The solution was then allowed to stand for 10 minutes to complete color development.

4.7. Nitrogen

4.7.1. Total Kjeldahl Nitrogen (TKN)

10 mL of the original sample was measured and transferred to a 250 mL round bottom flask, 10 mL of concentrated sulfuric acid, a catalyst pellet and glass beads were added. The flask was then placed in a heating blanket with the neck tilted 60 ° (see Figure 7). Heating was started at controlled temperature for a smooth boiling procedure. This process occurred to ensure a complete mineralization of the sample.



Figure 7. Balloon with drooping neck.

The mineralization was stopped after about an hour and a half, when the liquid was already clear, and the white smoke was gone. The flask could cool for 10 minutes and 50 mL of distilled water was added slowly with stirring.

In Figure 7 it is presented the experimental setup used to carry out the distillation. 50 mL of 40% NaOH was added to the flask to neutralize the acid and displace the ammonia. In a 200 mL Erlenmeyer flask, 50 mL of 4% boric acid and 3 drops of mixed indicator (methyl red/methylene blue) were charged to the exit of the distillation unit (see Figure 8). After the start of the process, the distillate was collected for 15 minutes. The distillate was titrated with 0,1M hydrochloric acid (HCl) (see Figure 9), and the equivalence point was established by the turn of color from green to slightly pinkish. By

the amount of HCl used in the titration the percentage of total nitrogen present in the sample was estimated.



Figure 8. Distillation unit.



Figure 9. Titration of the distillate.

This methodology for determination of total nitrogen was also used for sample Filtro 03/04. All analyzes were performed in triplicate.

4.7.2. Amoniactal Nitrogen

10 mL of the original sample was measured and transferred to a 200 mL round-bottom flask, 10 mL of concentrated sulfuric acid, a catalyst pellet and glass beads were added. This flask was placed on a heating blanket with the neck tilted 60 °. Heating was started at controlled temperature to ensure a smooth boiling process. This process occurred to promote the mineralization of the sample (see Figure 10).



Figure 10. Mineralization of the sample.

The mineralization was stopped after about an hour and a half, when the liquid was already clear, and the white smoke was gone. The mineralized solution was titrated with 0,1M hydrochloric acid (HCl). Again, the equivalence point was detected by a color change from green to slightly pinkish.

This methodology for determination of ammoniacal nitrogen was also used for sample Filtro 03/04. All analyzes were performed in triplicate.

4.8. Heavy metals

The analysis of heavy metals was performed for all samples under study. First, a mixture was prepared of 2 mL of 65% nitric acid and 6 mL of 37% hydrochloric acid. Then 5 mL of this mixture was added to a further 5 mL of sample. The reactor (see Figure 11) was sealed and brought to the oven at 60 °C for 48 hours to perform digestion.



Figure 11. Reactor used to digestion of the sample.

After completion of the digestion, the product in the reactor was filtered using a 0,45-micron syringe filter into a 50 mL volumetric flask. This solution was further diluted with 5% nitric acid (see Figure 12) and brought to refrigeration.



Figure 12. Samples after digestion, ready to be read on atomic absorption equipment.

4.8.1. Preparation of standard solution for quantification of heavy metals through atomic absorption

For quantification of the heavy metals through atomic absorption, it was necessary to prepare standard solutions. The quantified metals were: cadmium, lead, nickel and chromium. To prepare the initial concentration solution, which would be used for the preparation of other concentrations, a salt of each metal was used.

Cadmium sulfate A.R. grade ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) was used for cadmium analysis, to prepare the initial solution with a concentration of 100 ppm.

The preparation of the initial concentration of lead standard solution was carried out with lead in a 100 mL flask, in order to achieve the concentration of 100 ppm.

Nickel was used for the preparation of the initial solution of 100 ppm in a 100 mL flask.

Preparation of the initial chromate solution was performed using A.R. grade potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), the desired concentration was 100 ppm for a 100 mL flask.

The stock solution of potassium was prepared with potassium chloride KCl A.R. grade, to reach the concentration of 1000 ppm in a 200 mL flask. The atomic absorption equipment used in the methodology of preparing the potassium standard requires that the standards and samples to be analyzed have a concentration of cesium chloride of 1000 mg/L, so that 0,5 g of Cesium chloride and dilution in 5% nitric acid was performed, increasing in 250 mL. After this preparation, 10 mL of the solution with cesium chloride and 10 mL of sample or standard potassium solution.

The stock solution of copper was prepared using Copper metal strip. 1000 g of copper metal was dissolved in a minimum volume of 1:1 nitric acid and diluted to 1 L to obtain 1000 $\mu\text{g}/\text{mL}$ of Cu.

The standard zinc solution was prepared using zinc metal granules. 1000 g of zinc was dissolved in 40 mL of 1:1 hydrochloric acid and diluted to 1 L to obtain 1000 $\mu\text{g}/\text{mL}$ of zinc.

The European Union legislation stipulates limits for the metals Mercury, Arsenic and Biuret; however, to date these analyzes have not been carried out due to the lack of adequate equipment.

The other standard solutions were prepared from each stock solution described above. The concentrations produced are shown in Table 6.

Table 6. Concentrations for standard solutions of heavy metals.

Atomic Absorption Analysis Leachate					
Cd		Ci=100ppm		Legis. UE = 3ppm	
Conc. (ppm)	0,02	0,5	1,5	2	3
Vi (mL)	0,02	0,5	1,5	1	1,5
Pb		Ci=100ppm		Legis. UE = 120ppm	
Conc. (ppm)	0,1	0,25	0,5	10	30
Vi (mL)	0,1	0,25	0,5	5	15
Ni		Ci=100ppm		Legis. UE = 50ppm	
Conc. (ppm)	1	5	10	50	100
Vi (mL)	1	5	5	25	50
Cr (VI)		Ci=100ppm		Legis. UE = 2ppm	
Conc. (ppm)	0,06	1	2	5	15
Vi (mL)	0,06	0,5	1	2,5	7,5
K		Ci=1000ppm		Legis. UE = 20000ppm	
Conc. (ppm)	100	200	400	600	800
Vi (mL)	5	10	20	30	40
Cu		Ci=1000ppm		Legis. UE = 600ppm	
Conc. (ppm)	10	100	300	600	1000
Vi (mL)	1	5	15	30	50
Zn		Ci=3000ppm		Legis. UE =1500ppm	
Conc. (ppm)	150	600	1500	2100	3000
Vi (mL)	5	10	25	35	50

The calibration curves used for each heavy metal are shown in Figure 13.

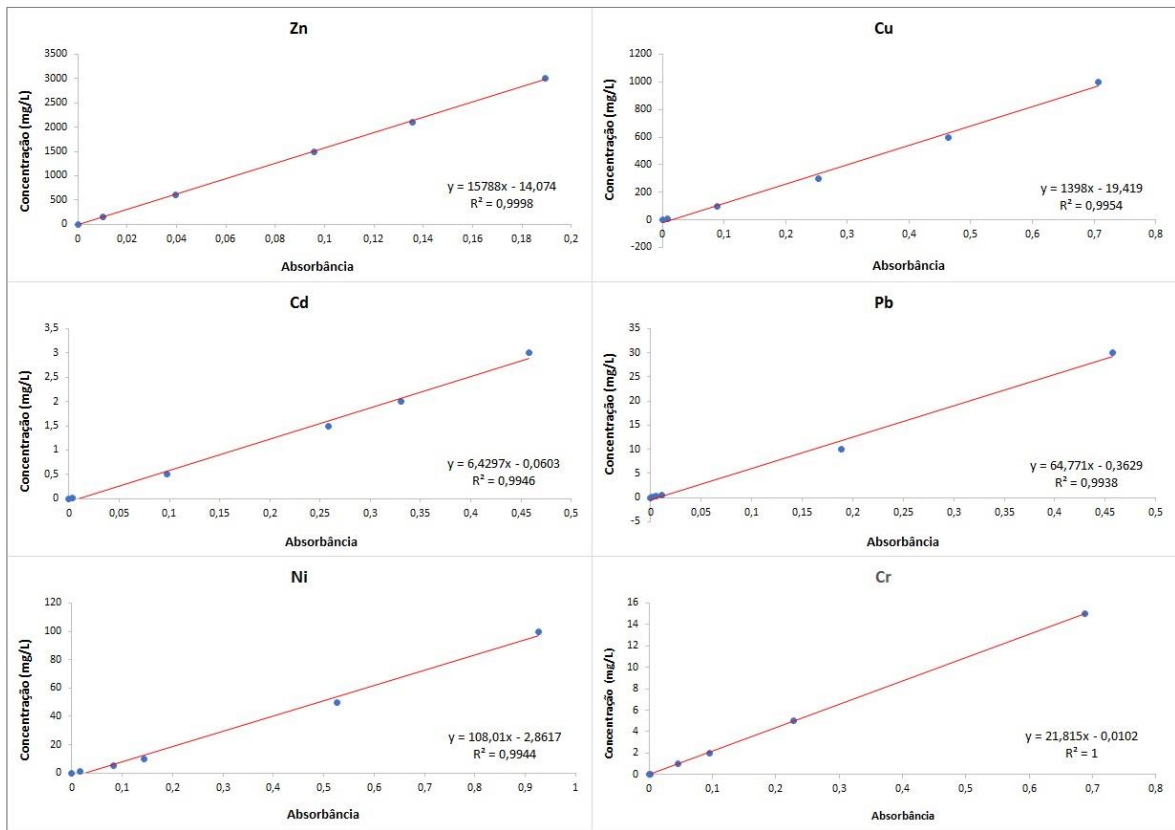


Figure 13. Calibration curve of metals Zn, Cu, Cd, Pb, Ni and Cr.

4.9. Tests of adsorbents produced locally

The Filtro 03/04 sample was later treated with two different types of adsorbents produced at the Polytechnic Institute of Bragança.

4.9.1. Activated carbon obtained from compost

The first one was obtained through the compound recovered from the composting process of the company Resíduos do Nordeste, EIM, the same company that supplied the original effluent sample for this work. The compost was washed with distilled water, dried in a furnace for 12h at 110 °C, powdered and sifted, with the intention of homogenizing the compost.

Different amounts of the organic compound were mixed with distilled water to obtain different initial concentrations. The reaction vessel was then inserted in an oven at three pre-set temperatures, which differentiated the samples from each other. After reaching the desired reaction time, the samples were cooled to room temperature for up to 24 h. The solids were separated by vacuum filtration with 0,45 μm pore filter, washed with distilled water and dried for 12-15 h at 100 °C.

This process resulted in the production of 3 different adsorbents of the same origin. The activated carbons "10" and "11" were baked at 230 °C for 4 and 2 hours, respectively. The "12" sample had its thermal treatment at 150 °C, for a period of 2 hours.

For each adsorbent, two different masses were used for the tests, resulting in six tests. Six erlenmeyers were used with 10 mL of the 3/4 Filtro sample each. 0,1g and 0,2g of each activated carbon sample was weighed and added to the Erlenmeyer. The six sample vials and the adsorbents were placed on a shaking plate for 48 hours, as shown in Figure 14.

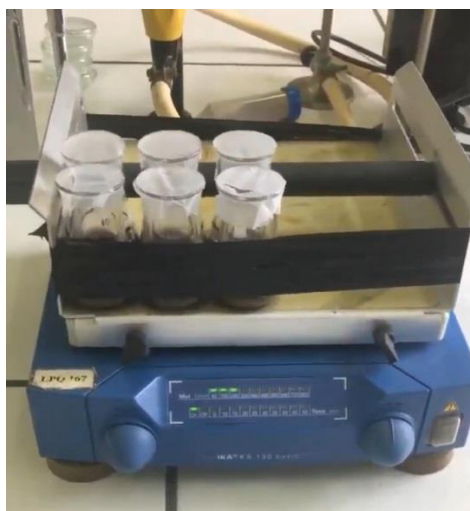


Figure 14. Agitation plate with the Filtro 03/04 sample and the adsorbents under test.

After this period of 48 hours, the treated samples were taken to the centrifuge for 20 minutes, in 10000 rpm, to separate the solids from treated effluent. These samples were stored in individually in labeled plastic bottles, as shown in Figure 15, for further analyzes of parameters that could influence the quality of the liquid fertilizer.

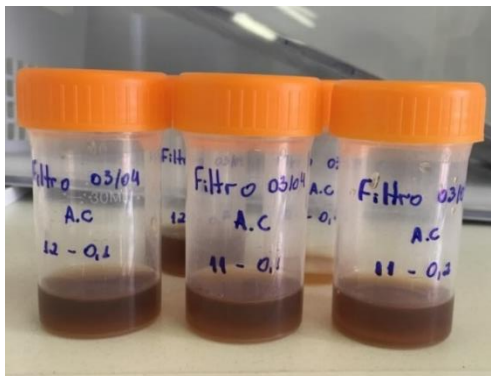


Figure 15. Samples treated with adsorbents.

4.9.2. Adsorbent obtained by clay activation

The second test was performed with adsorbents also produced in the IPB, obtained through the activation of clay samples.

Four clays originating in Kazakhstan were taken from Karatau (KAN), Akzhar (AKN), Kokshetau (KON) and Asa (ASN) deposits and were used as feedstocks to prepare activated clays.

The clays were activated with acid. 150 mL of 4 M H_2SO_4 was heated at 80 °C in a three-neck round bottom flask. When the system temperature stabilized, 3 g of natural sample was added to the flask. The resulting suspension was stirred at 80 °C for 3 h. After cooling the dispersion, the suspension was filtered, and the supernatant discharged. The activated clay was washed repeatedly until the wash water reached a pH near the natural pH, which is 7. The material was recovered and then dried in a static air oven at 60 °C overnight to obtain the samples AKA, ASA, KAA and KOA, activated clays of AKN, ASN, KAN and KON, respectively (Silva A. S., 2019).

The samples provided are shown in Figure 16.

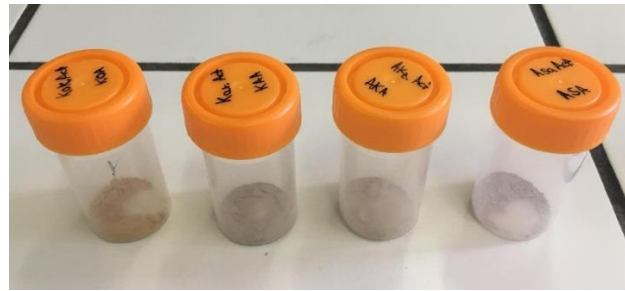


Figure 16. Clay adsorbents.

For each sample, 0,1g and 0,2g were weighed, and eight samples of filtered effluent treated with these adsorbents were obtained. The masses were placed in eight erlenmeyers (see Figure 17) with 20 mL of filtered effluent each. The erlenmeyers were left on shaken for 48 hours (see Figure 18), then, the treated samples were taken to the centrifuge for 20 minutes, in 10000 rpm, to separate the solids from treated effluent. The treated samples were refrigerated for further analysis.



Figure 17. Different masses of clay adsorbent.



Figure 18. Samples being treated with shaking.

5. Results and discussion

5.1. Total Organic Carbon

One of the main parameters that must be present in liquid fertilizers is organic carbon, this parameter is directly related to the amount of organic matter present in the fertilizer. According to the European Parliament and the Council (2019), this ratio is given by:

$$C_{org} = \text{organic matter} \times 0,56 \quad (1)$$

The regulation approved in 2019 states that to be considered liquid organomineral fertilizer, the product must contain at least 3% of organic carbon, and 5% for organic fertilizer liquid, in this way, Table 7 presents the values of total organic carbon in mg/L found for samples: Original, Filtro 03/04, 1,19× and 1,85×. Table 8 shows the percentages that will be used for comparison with legislation.

Table 7. Amount of Total Organic Carbon present in the samples with and without dilution.

Sample	TOC (mg/L) dilution	TC (mg/L) dilution	IC (mg/L) dilution	TOC (mg/L)	TC (mg/L)	IC (mg/L)
Original 500x	56,26	61,03	4,77	28130	30515	2385
Filtro 03/04	55,84	59,19	3,35	27920	29595	1675
1,19x 500x	65,33	68,69	3,36	32665	34345	1680
1,85x 500x	107,23	110,3	3,05	53615	55150	1525

Table 8. Percentage of Total Organic Carbon present in the samples.

Sample	% TOC	% TC	% IC
Original 500x	2,813 ± 3,79E-4	3,051 ± 2,31E-4	0,238 ± 1,55E-5
Filtro 03/04	2,792 ± 1,51E-3	2,959 ± 1,64E-3	0,167 ± 2,55E-6
1,19x 500x	3,266 ± 1,13E-2	3,434 ± 1,15E-2	0,168 ± 4,66E-7
1,85x 500x	5,361 ± 1,88E-3	5,515 ± 2,00E-3	0,152 ± 4,41E-6
Liquid Organomineral Fertilizer (EU, 2019)	3,00		---
Organic Liquid Fertilizer (EU, 2019)	5,00		---

It is observed that the original sample reaches close to 3% of TOC required by European legislation, however, this value is slightly reduced when filtering this leachate with the sole intention of removing the solids, it can be stated in this way that the total organic carbon is mostly present in the liquid part of the leachate, which is interesting since the intention is to use it as a liquid fertilizer.

The concentration procedure was performed by simple distillation to remove the small excess of water in the samples and meet the minimum requirements.

The filtered sample only 1,19× and has already reached the minimum required by the European Parliament and the Council (2019). The Filtro 03/04 sample was again subjected to a distillation process, this time a little longer, so that the value of 5% TOC for liquid organic fertilizers could be reached, even for this percentage, the necessary concentration was considered relatively low, being only 1,85×.

5.2. Density

The density of the samples was measured and are presented in Table 9.

Table 9. Density of the samples.

Samples	Density 20 °C (g/cm³)
Original	1,032
Filtro 03/04	1,030
1,19x	1,035
1,85x	1,056

The density showed low variations between the samples.

It is observed a slight increase in this parameter, for the 1,85× sample, due to loss of water during the concentration process, leaving the sample with the highest solids concentration.

It was also observed that the total organic carbon content has a great influence on the density of the samples. In this way a statistical analysis was used to verify this correlation between TOC and sample density.

Figure 19 shows how the density is affected by the presence of TOC.

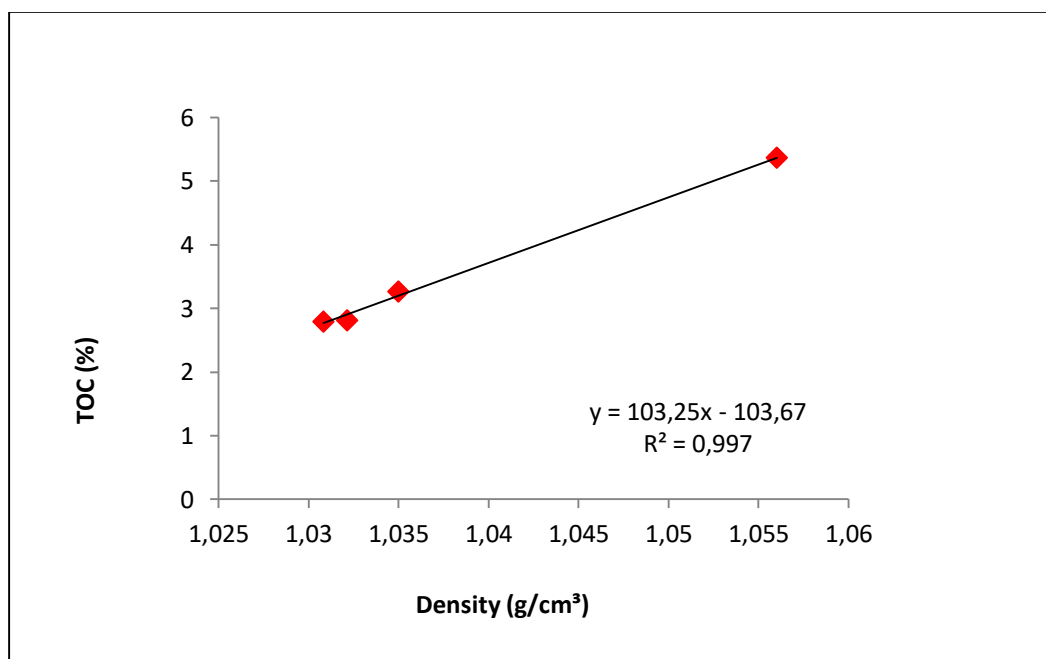


Figure 19. Correlation between TOC and Density.

Note that with higher percentage of total organic carbon, the density increases slightly, with an exponential increase trend. A significance test, Pearson's correlation coefficient, was then applied. Pearson's correlation coefficient measures the degree of correlation (and the direction of this correlation - whether positive or negative) between two metric scale variables. This coefficient, usually represented by ρ , only assumes values between -1 and 1 (Figueiredo Filho & Silva Junior, 2009).

$\rho = 1$, means a perfect positive correlation between the two variables.

$\rho = -1$ It means a perfect negative correlation between the two variables, that is, if one increases, the other always decreases.

$\rho = 0$, means that the two variables do not depend linearly on each other.

A correlation coefficient $\rho = 0,998479$ was obtained for the samples. Thus, it can be stated that the correlation between density and TOC values is statistically significant for a 99% confidence interval.

5.3. pH and Conductivity

In the distillation process, due to the removal of water, also occurs the concentration of inorganic carbon content, such as carbonates, which must be corrected to a neutral pH before a possible use as fertilizer. Table 10 shows the measured pH and conductivity values for the samples.

Table 10. pH and conductivity of samples at 20° C.

Samples	Temperature (°C)	pH	Conductivity (mS/cm)	% IC
Original	20	7,53	39	$0,238 \pm 1,55E-5$
Filtro 03/04	20	7,81	40	$0,167 \pm 2,55E-6$
1,19x	20	7,98	38,8	$0,168 \pm 4,66E-7$
1,85x	20	6,55	52,3	$0,152 \pm 4,41E-6$

The pH and conductivity of the samples did not show high variations between the original, Filtro 03/04 and concentrated samples, it was expected that the 1,85× sample, which is the most concentrated, had a higher pH value than the samples as well as conductivity, however, it is observed that the pH values follow the inorganic carbon content, which presents the carbonates and bicarbonates present in the samples.

Electric conductivity is used to measure the amount of salts present in soil solution. The greater the amount of salts present in the solution, the greater the value of electrical conductivity obtained. Excess salts in the root zone, regardless of ions present, impair plant germination, development and productivity. This is because a higher concentration of the solution requires more energy from the plant to absorb water (Brandão, 2002).

5.4. Dry matter and Ash

The dry matter, often also referred to as Total Solids (TS), is the term used for the material remaining in the crucible after evaporation of sample water and subsequent drying in the oven at 105 °C.

When this residue is calcined at 450 °C, the organic substances volatilize and the minerals remain as ash, thus forming the total volatile solid (TVS) and the total fixed solids (TFS).

The TFS form the inorganic fraction that compose the leachate, having as main constituents the inorganic minerals (calcium, potassium, carbonates, sulfates, among others). Table 11 shows the dry matter and ash values of the samples under study. The analyzes were performed to quantify TS and TFS contents. For the calculation of TVS, the difference between the total and fixed solids was made (see Table 12).

Table 11. Percentage of dry mass and ash in samples.

Dry matter						
Samples	crucible mass (g)	full (g)	dry (g)	inicial mass (g)	dry matter (g)	% dry matter
Original	39,16	41,86	39,33	2,70	0,17	6,46 ± 0,07
Filtro 03/04	35,80	37,48	35,90	1,68	0,10	6,03 ± 0,04
1,19x	41,75	43,38	41,86	1,63	0,11	7,07 ± 0,27
1,85x	35,87	37,10	36,01	1,23	0,14	11,50 ± 0,25

Ash						
Samples	crucible mass (g)	full (g)	dry (g)	inicial mass (g)	Ash (g)	% Ash
Original	33,80	36,42	33,88	2,61	0,08	3,07 ± 0,25
Filtro 03/04	35,01	37,10	35,07	2,09	0,06	2,96 ± 0,13
1,19x	35,91	37,02	35,94	1,11	0,03	2,94 ± 0,05
1,85x	36,16	37,09	36,21	0,93	0,05	5,59 ± 0,02

Table 12. Percentage of Total volatil solids.

Samples	% dry matter	% Ash	% TVS
Original	6,46	3,07	3,39
Filtro 03/04	6,03	2,96	3,07
1,19x	7,07	2,94	4,13
1,85x	11,50	5,59	5,91

Observing the values presented in Table 11, it can be verified that the dry matter contents do not have high variability between the original, Filtro 03/04 and 1,19x samples. The 1.85x sample has higher solids content due to the concentration process. It was possible to observe that the organic and inorganic fractions have smaller difference with the higher concentration of the samples.

The original and “Filtro 03/04” samples showed similar ash content and lower than the concentrated samples.

When the ash value is greater than the value of the TVS, then the fraction of inorganic matter prevails in relation to the fraction of organic matter that constitute the effluent.

Thus, for the original and “Filtro 03/04” samples, the organic matter fraction is higher, whereas in the concentrated samples the predominant fraction is inorganic. This is because, for the concentration of these samples, it was necessary to raise the temperature, that is, portions of the organic contents were volatilized.

The importance of measuring this parameter is therefore, according to Oliveira *et al.* (2000), irrigation with liquids containing high concentrations of solids can cause changes in the water infiltration capacity in the soil, caused by the clogging of macropores and the formation of crusts on its surface. The formation of superficial crusts causes infiltration problems.

5.5. Phosphorus

After the preparation of the samples and standards, none of the samples were determined to contain the minimum concentration required for the absorbance equipment to read, that is, the samples had values lower than the lowest calibration curve standard value (<20 ppm).

These values denote a low concentration of P₂O₅ in the sample collected from the supernatant residue in the storage tank.

The figures are below the minimum required by legislation, even in more concentrated samples, since the Regulation of the European Parliament and of the Council (2019) provides that an organomineral fertilizer must contain at least one of the declared primary nutrients: N, P₂O₅, K₂O. And when this fertilizer contains only one of these nutrients, in the case of P₂O₅, the minimum concentration should be 2% by mass of total phosphorus pentoxide (P₂O₅).

5.6. Nitrogen

The procedure for the characterization of nitrogen was carried out to obtain the parameters of the leachate, in order to compare it with the current legislation, aiming the conformity for its use as liquid organomineral fertilizer.

The results obtained from ammoniacal nitrogen, total nitrogen and by difference, organic nitrogen, are shown, respectively, in Tables 13, 14 and 15.

Table 13. Amount of ammoniacal nitrogen present in the samples.

Ammoniacal Nitrogen			
Samples	HCl (mL)	NH₃ (mg/L)	% mass
Original	5,22	289,28	0,03
Filtro 03/04	3,40	188,54	0,02

Table 14. Amount of total nitrogen present in the samples.

TKN			
Samples	HCl (mL)	NH₃ (mg/L)	% mass

Original	24,43	4064,68	0,41
Filtro 03/04	23,07	3837,32	0,38

Table 15. Amount of organic nitrogen present in the samples.

Nitrogen organic		
Samples	NH ₃ (mg/L)	% mass
Original	3775,39	0,38
Filtro 03/04	3648,78	0,36

This analysis was applied only to the original and Filtro 03/04 samples that present the maximum possible value for the leachate. The concentrated samples were not analyzed because with the distillation process some amount of volatile nitrogen is lost due to the heating process. Therefore, the N content for the concentrated slurry samples should be underestimated.

According to the Parliament and Council Regulation (2019), to be considered as a liquid organomineral fertilizer, the product must contain at least one of the nutrients declared in the minimum quantities, which for nitrogen is: 2% by weight of total nitrogen, of which 0,5% by mass of the fertilizer product should be organic nitrogen.

Therefore, the nitrogen values do not meet the requirements of the legislation. Thus, it was necessary to carry out the potassium analysis, for comparison with the legislation and possible compliance with at least one of the necessary nutrients, so that the leachate can be used as a liquid organomineral fertilizer.

5.7. Heavy Metals

The concentration of heavy metals is shown in Table 16.

Table 16. Comparison of the values of heavy metals recommended by the European legislation and the values found in the samples, for use as commercial fertilizer.

Samples	Zn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cr (mg/kg)
EU 2019	1500	600	3	120	50	2
Original	468,60	101,60	0,37	4,76	116,33	10,74
Filtro 03/04	252,80	241,10	0,91	4,11	148,93	9,83
1,19×	1077,60	56,07	0,69	15,77	155,51	11,08
1,85×	1299,80	11,30	0,41	11,01	62,81	10,47

It is noted that the heavy metals zinc, cadmium, copper and lead found in the samples are all below the limit values set by European legislation. However, it is observed that the results are not cohesive, since it is assumed that in concentrated samples, the values of heavy metals would be higher, and this was not confirmed in all metals. This discrepancy is suggested due to the minimum reading range of the atomic absorption equipment, which equipment does readings in ppm, that is, the values of these metals are below the minimum reading range of the equipment, in this way, it is known that limits are not achieved, however, it is not possible to determine the exact concentration of each metal. New analyzes must be performed on atomic absorption equipment with capacity for ppb readings, in order to determine the exact concentration of each heavy metal in the leachate under study.

The detection limit (LD) of an analytical method corresponds to the smallest amount of an analyte that can be detected but not necessarily quantified as an exact value. In the case of quantitative methods, it may not be essential to estimate this parameter, since the greatest interest is in knowing which is the smallest amount that can be quantified. However, its determination is usual. The quantification limit (LQ) corresponds to the smallest amount of an analyte that can be determined quantitatively with adequate accuracy using an experimental procedure. The quantification below the LQ is not acceptable. Therefore, results below this value should only be expressed as semiquantitative or qualitative (Mustra, 2009).

For nickel and chromium, it was observed that all the samples exceeded the maximum values allowed by the European Union, so a treatment of this leachate is necessary to reduce the concentration of these metals so that it can be marketed as liquid organomineral fertilizer.

Excess chromium and nickel can cause diverse negative adversities to human health and the environment.

Chromium is bioaccumulative, therefore, special care is requiring both in handling of chromium compounds as well in the treatment of generated waste. Exposure to hexavalent chromium may occur, generally through inhalation, skin contact and ingestion. In addition to cancer, exposure may cause allergic dermatitis, skin ulcers, scars, and even perforations of the nasal septum (Cheis, 2013).

The presence of harmful amounts to the plants can result in damages such as chlorosis, reduction of leaf and root growth and death (Castro, 2014).

Soluble Ni salts and Ni sulfides and oxides are carcinogenic to humans and may affect the lungs and nasal tissues. Because of its potential for toxicity, nickel may have as effects, after inhalation, chronic bronchitis, asthma, reduced vital capacity and pulmonary emphysema (Agency, 2009).

The solubility of Ni in the soil is influenced by the pH, the presence of organic matter and clays and manganese and iron ions in the soil, and the mobility of the nickel in the soil increases with the decrease of pH. Most Ni compounds are soluble at pH values below 6.5. Compared to other heavy metals such as Cd and Zn, Ni presents greater mobility in soils (Ribeiro, 2013).

According to the Environment Agency (2009), the plants have different Ni tolerance capacities, and the species with the greatest absorption capacity of this metal are Cruciferae (which includes turnip, cabbage and cauliflower) and Leguminosae (such as peas and bean).

It is then concluded that zinc, cadmium, copper and lead meet EU requirements in all samples analyzed, however, nickel and chromium must be removed.

From the characterization of the slurry samples, a flowchart for the appropriate treatment, with the intention of using the leachate as fertilizer, can now be proposed.

The concentration of biuret, arsenic and mercury were not determined due to the lack of materials for analysis, therefore, it is necessary to characterize this metal before asserting the use of the leachate as fertilizer.

5.8. Results and discussions of adsorbent tests

The results of the two leachate treatment tests with the three types of organic compound adsorbents and the four types of clays adsorbents are set forth below.

5.8.1. Test with adsorbent- Activated Carbon

The first test was carried out using the adsorbents from the organic compound provided by the same landfill company that supplied the leachate samples.

5.8.1.1. Total Organic Carbon

Analyzes were performed to determine the total organic carbon present in the samples, after being submitted to the treatment. Table 17 shows the TOC values provided by the analytical equipment, that is, with the diluted sample (1:500) and presents these values already converted to the actual value present in the leachate.

In Table 18, the percentage of total organic carbon present in the analyzed product can be observed, so that the values can be compared with the current legislation.

Table 17. Total organic Carbon of treated samples with activated carbon.

Sample	TOC (mg/L) dilution	TC (mg/L) dilution	IC (mg/L) dilution	TOC (mg/L)	TC (mg/L)	IC (mg/L)
10- 0,1	40,52	43,56	3,04	20261,67	21780,00	1519,83
11- 0,1	39,65	42,54	2,89	19825,00	21268,33	1443,17
12- 0,1	40,42	43,21	2,80	20208,33	21606,67	1399,00
10- 0,2	46,00	49,04	3,04	22998,33	24520,00	1522,33
11- 0,2	47,13	49,85	2,72	23563,33	24925,00	1361,00
12- 0,2	41,47	43,99	2,53	20733,33	21996,67	1262,50

Table 18. Percentage of total organic Carbon of treated samples with activated carbon.

Sample	% TOC	% TC	% IC
Filtro 03/04	$2,79 \pm 1,88E-3$	$2,96 \pm 2,00E-3$	$0,17 \pm 1,55E-5$
10- 0,1	$2,03 \pm 5,88E-4$	$2,18 \pm 6,75E-4$	$0,15 \pm 2,70E-6$
11- 0,1	$1,98 \pm 9,08E-4$	$2,13 \pm 9,98E-4$	$0,14 \pm 2,16E-6$
12- 0,1	$2,02 \pm 2,12E-4$	$2,16 \pm 2,21E-4$	$0,14 \pm 2,09E-7$
10- 0,2	$2,30 \pm 1,78E-4$	$2,45 \pm 1,93E-3$	$0,15 \pm 2,26E-6$
11- 0,2	$2,36 \pm 4,84E-4$	$2,49 \pm 5,10E-4$	$0,14 \pm 4,46E-7$
12- 0,2	$2,07 \pm 5,27E-4$	$2,20 \pm 5,61E-4$	$0,13 \pm 2,89E-7$

The regulation of the European Parliament and the Council (2019), stipulates that for a fertilizer to be classified as a liquid organomineral, it must contain at least 3% of TOC.

The samples treated with the activated carbon presented values lower than the provisions of the regulation, which was already expected, since the sample Filtro 03/04, which was treated, had only 2,8% TOC.

However, it is observed that with increasing mass of the same type of adsorbent, a slight increase in the percentage of TOC occurs as well. This may have occurred due to the origin of the adsorbent.

It is expected that this increase in TOC would occur, because it is probable that the adsorbent will leach some species that were analyzed, in this way, there are exchanges between the solid and the liquid.

Activated carbon 11-0,2 was the most leaching of this component for the samples, in relation to the other adsorbents of this origin.

5.8.1.2. Density

The density of the samples treated with the activated carbon did not change in relation to the sample Filtro 03/04, which was used for the treatment, therefore, for the evaluations of these results, the value previously measured was assumed, 1,03g/cm³.

5.8.1.3. *pH and Conductivity*

The pH and conductivity of the samples treated with this adsorbent did not show significant changes that influenced leachate characteristics after treatment.

5.8.1.4. *Dry matter and Ash*

The dry matter, or total solids, was quantified by mass and percentage, as well as ash analyzes, or fixed solids. The measurements are set out in Tables 19 and 20, respectively.

Table 19. Percentage of dry matter of treated samples with activated carbon.

Dry matter						
Samples	crucible mass (g)	full (g)	inicial mass (g)	dry (g)	dry matter (g)	% dry matter
Filtro 03/04	35,80	37,48	1,68	35,90	0,10	6,03
10- 0,1	36,26	37,46	1,20	36,34	0,08	6,33
11- 0,1	35,36	36,53	1,17	35,43	0,07	5,74
12- 0,1	38,19	39,22	1,03	38,26	0,06	5,97
10- 0,2	35,11	36,67	1,56	35,20	0,09	5,86
11- 0,2	36,30	37,84	1,53	36,39	0,09	5,60
12- 0,2	37,94	39,47	1,54	38,02	0,09	5,68

It is observed that the percentage of dry matter has little variation among the samples tested. There was a slight reduction of the total solids of the Filtro 03/04 sample for the samples treated with the adsorbents, with the exception of 10-0,1, this increase of solids in this case may have occurred due to the separation of the activated carbon from the sample, after the treatment, has not been carried out in order to eliminate all the adsorbent.

Table 20. Percentage of ash of treated samples with activated carbon.

Ash						
Samples	crucible mass (g)	full (g)	inicial mass (g)	dry (g)	Ash (g)	% Ash
Filtro 03/04	35,00	37,09	2,09	35,07	0,06	3,00
10-0,1	36,26	37,46	1,20	36,30	0,04	3,00
11-0,1	35,36	36,53	1,17	35,40	0,03	2,90
12-0,1	38,19	39,22	1,03	38,22	0,03	2,91
10-0,2	35,11	36,67	1,56	35,15	0,04	2,90
11-0,2	36,30	37,84	1,53	36,34	0,04	2,64
12-0,2	37,94	39,47	1,54	37,98	0,04	2,77

With the difference between the dry matter and the ash, the equivalent value of the volatile solids was obtained, these data can be found in Table 21.

Table 21. Percentage of total volatil solids of treated samples.

Samples	% dry matter	% Ash	TVS (%)
Filtro 03/04	6,03	3,00	3,03
10-0,1	6,33	3,00	3,33
11-0,1	5,74	2,90	2,84
12-0,1	5,97	2,91	3,06
10-0,2	5,86	2,90	2,96
11-0,2	5,60	2,64	2,96
12-0,2	5,68	2,77	2,91

Through Table 21, show that the percentage of total volatile solids was higher for most of the adsorbents tested, except for a small difference in the sample 11-0,1.

This indicates that the leachate treated with activated carbon has a higher fraction of organic matter than of inorganic matter in its composition.

5.8.1.5. Phosphorus

No analyzes were carried out for quantification of the phosphorus nutrient, since the initial analysis made for the original sample had a lower value for this nutrient, so after

the treatment with the adsorbents, it was known that this value would not be legally enough for a liquid organomineral fertilizer classification.

5.8.1.6. Nitrogen

Total ammoniacal and organic nitrogen analyzes were not performed for the samples treated with the adsorbents under test, since the original sample and the Filtro 03/04 had already shown values below that required for liquid organomineral fertilizers, that is, there was no need of quantification of this nutrient after the treatment with the adsorbent, since it was already known that the value would not exceed the stipulated by the legislation.

5.8.1.7. Heavy Metals

As shown above, for the Original, Filtro 03/04 and concentrated samples, chromium and nickel metals did not meet the values determined by the legislation.

In this way, this treatment was carried out with activated carbon in order to adsorb heavy metals from the leachate.

Table 22 shows the results of heavy metals provided by the atomic absorption equipment.

Table 22. Heavy metals quantified in the treated samples with activated carbon.

Samples	Zn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cr (mg/kg)
EU 2019	1500	600	3	120	50	2
Filtro 03/04	252,10	241,10	0,91	4,11	148,93	9,83
10-0,1	480,93	250,26	0,77	3,91	11,14	6,35
10-0,2	259,73	22,53	1,35	1,06	132,40	6,50
11-0,1	265,20	253,00	1,06	1,08	131,67	7,00
11-0,2	543,56	306,42	0,65	1,10	158,33	6,80
12-0,1	254,97	309,58	1,02	1,04	3,38	7,44
12-0,2	268,01	23,24	0,53	1,09	101,13	8,94

Data presented previously show that only Chromium and Nickel metals do not meet the limits stipulated by the legislation. However, for the other metals, it was observed that there was an increase in the obtained concentration data, in relation to the sample before the treatment.

The obtained data do not provide consistency between them, two hypotheses are suggested as possible sources of this problem. The first would be that the adsorbent used, that is, the activated carbon, has leached heavy metal components (since it originates from a compound that has these metals) during the adsorption process. The second hypothesis would be the fact that the data obtained are below the smallest point of the calibration curve of the atomic absorption equipment, thus, although it shows that the values are below the limits, the reading is not accurate as to the real value of the metals present in the leachate.

5.8.2. Test with adsorbent - Clays

Four adsorbents originating from the clays were tested in two different masses each, totaling eight tests. The results found in the analyzes are presented below.

5.8.2.1. *Total Organic Carbon*

Table 23 presents the values of total organic carbon in mg/L and, Table 24 shows the percentage of TOC corresponding to the leachate under study after treatment with the clay adsorbents.

Table 23. Total organic Carbon of treated samples with adsorbent of Clays.

Sample	TOC (mg/L) dilution	TC (mg/L) dilution	IC (mg/L) dilution	TOC (mg/L)	TC (mg/L)	IC (mg/L)
ASA- 0,1	49,62	52,83	3,20	24810,00	26415,00	1602,17
ASA- 0,2	48,18	51,25	3,07	24091,67	25626,67	1533,67
KAA- 0,1	47,85	51,05	3,20	23923,33	25525,00	1602,33
KAA- 0,2	50,18	53,47	3,29	25091,67	26735,00	1644,00
AKA- 0,1	47,81	51,06	3,25	23905,00	25528,33	1622,50
AKA- 0,2	47,51	49,87	2,63	23756,67	24936,67	1314,17
KOA- 0,1	47,44	50,31	2,86	23720,00	25153,33	1432,17
KOA- 0,2	50,34	53,31	2,97	25171,67	26655,00	1484,33

Table 24. Percentage of total organic carbon of treated samples with adsorbent of Clays.

Sample	% TOC	% TC	% IC
Filtro 03/04	2,79 ± 1,88E-3	2,96 ± 2,00E-3	0,16 ± 4,41E-6
ASA- 0,1	2,48 ± 3,65E-4	2,64 ± 3,98E-4	0,16 ± 6,01E-7
ASA- 0,2	2,41 ± 1,51E-3	2,56 ± 1,65E-3	0,15 ± 2,35E-6
KAA- 0,1	2,39 ± 7,19E-4	2,55 ± 7,85E-4	0,16 ± 1,43E-6
KAA- 0,2	2,51 ± 1,63E-3	2,67 ± 1,76E-3	0,16 ± 9,96E-7
AKA- 0,1	2,39 ± 1,76E-3	2,55 ± 1,91E-3	0,16 ± 2,81E-6
AKA- 0,2	2,38 ± 1,15E-3	2,49 ± 8,14E-4	0,13 ± 5,31E-7
KOA- 0,1	2,37 ± 7,13E-4	2,51 ± 7,85E-4	0,14 ± 1,51E-6
KOA- 0,2	2,52 ± 1,64E-4	2,66 ± 1,80E-4	0,15 ± 2,00E-6

It is possible to observe that there was a slight reduction of the TOC content, in relation to the sample Filtro 03/04, after the treatment with the adsorbents.

It can be observed in the AKA sample that the increase in adsorbent mass did not influence the removal of TOC content, thus, it can be concluded that the removal reaches a constant value with a certain mass of activated clays.

The use of adsorbents is commonly used for the removal of heavy metals in effluents, however, the reduction of the total organic carbon content was already expected. It is indicated that there is a concentration of the leachate prior to treatment with adsorbents so that the final product contains at least 3% TOC, which is recommended by the Regulation of the European Parliament and of the Council, approved in May 2019, for liquid organomineral fertilizers.

5.8.2.2. *Density*

The density of the samples treated with the activated carbon did not change in relation to the sample Filtro 03/04, which was used for the treatment, therefore, for the evaluations of these results, the value previously measured was assumed, 1,03g/cm³.

5.8.2.3. *pH and Conductivity*

The pH and conductivity of the samples treated with this adsorbent did not show significant changes that influenced leachate characteristics after treatment.

5.8.2.4. *Dry matter and Ash*

Total solids (TS) and fixed solids (TFS) analyzes were performed for the clay adsorbent samples tested (Table 25 and 26). The difference between TS and TFS, gives the value of the volatile solids present in the leachate sample, after treatment (see Table 27), i.e. the fraction of organic compounds.

Table 25. Percentage of dry matter of treated samples with adsorbents of clays.

Dry matter						
Samples	crucible mass (g)	full (g)	inicial mass (g)	dry (g)	dry matter (g)	% dry matter
Filtro 03/04	35,80	37,48	1,68	35,90	0,10	6,03
ASA 0,1	35,29	36,78	1,49	35,38	0,09	6,07
KOA 0,1	37,60	38,73	1,13	37,66	0,06	5,65
KAA 0,1	36,87	38,78	1,90	36,99	0,11	5,90
AKA 0,1	36,30	37,68	1,38	36,38	0,08	5,89
ASA 0,2	39,25	41,08	1,82	39,36	0,11	5,93
KOA 0,2	31,31	33,47	2,16	31,43	0,13	5,83
KAA 0,2	35,11	36,81	1,70	35,21	0,10	5,96
AKA 0,2	38,19	39,95	1,76	38,28	0,09	5,38

Table 26. Percentage of ash of treated samples with adsorbents of clays.

Ash						
Samples	crucible mass (g)	full (g)	inicial mass (g)	dry (g)	Ash (g)	% Ash
Filtro 03/04	35,01	37,10	2,09	35,07	0,06	2,99
ASA 0,1	35,29	36,78	1,49	35,34	0,05	3,15
KOA 0,1	37,60	38,73	1,13	37,63	0,03	2,75
KAA 0,1	36,88	38,78	1,90	36,93	0,06	2,95
AKA 0,1	36,30	37,68	1,38	36,34	0,04	2,99
ASA 0,2	39,25	41,08	1,82	39,30	0,05	2,86
KOA 0,2	31,31	33,47	2,16	31,38	0,06	2,84
KAA 0,2	35,11	36,81	1,70	35,16	0,05	2,98
AKA 0,2	38,19	39,95	1,76	38,24	0,05	2,81

The content of total solids and ash has little variation among the samples treated with the clay adsorbents. For the most part, the treated samples have a lower amount of TS and TFS than the Filtro 03/04 sample. There is only one exception, the adsorbent ASA 0,1, which presented the percentage of dry matter and ash slightly larger, this may have occurred by remnants of solid at the time of separation of the adsorbent from the sample.

Using the TS and TFS data, the volatile solids content was calculated. Table 27 shows the corresponding values.

Table 27. Percent volatile solids of samples treated with clay adsorbent.

Samples	% dry matter	% Ash	TVS (%)
Filtro 03/04	6,03	3,00	3,03
ASA 0,1	6,07	3,15	2,92
KOA 0,1	5,65	2,75	2,90
KAA 0,1	5,90	2,95	2,95
AKA 0,1	5,89	2,99	2,90
ASA 0,2	5,93	2,86	3,07
KOA 0,2	5,83	2,84	2,99
KAA 0,2	5,96	2,98	2,98
AKA 0,2	5,38	2,81	2,57

In Table 27, through the contents of fixed solids and volatile solids, it is noted that there is little difference between the organic and inorganic fractions of samples treated with activated clay, presenting relatively constant values after treatment.

5.8.2.5. *Phosphorus*

No analyzes were carried out for quantification of the phosphorus nutrient, since the initial analysis made for the original sample had a lower value for this nutrient, so after the treatment with the adsorbents, it was known that this value would not be legally allowed for liquid organomineral fertilizers.

5.8.2.6. *Nitrogen*

Total ammoniacal and organic nitrogen analyzes were not performed for the samples treated with the adsorbents under test, since the original sample and the Filtro 03/04 had already shown values below that required for liquid organomineral fertilizers, that is, there was no need of quantification of this nutrient after the treatment with the adsorbent, since it was already known that the value would not exceed the stipulated by the legislation.

5.8.2.7. *Heavy Metals*

Heavy metals are usually found in raw effluents, and in the case of landfill effluents, the concentration of this parameter may have variability. In this context, tests were carried out with adsorbents to remove these pollutants.

Table 28 presents the values obtained through atomic absorption, for the Filtro 03/04 sample, after the treatment with the clay adsorbents.

Table 28. Heavy metals quantified in the treated samples with adsorbents of clays.

Samples	Zn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cr (mg/kg)
EU 2019	1500	600	3	120	50	2
Filtro 03/04	252,10	241,10	0,91	4,11	148,93	9,83
ASA 0,1	250,51	195,53	0,70	4,07	61,36	8,35
KAA 0,1	1077,58	140,18	0,86	1,09	19,62	14,60
AKA 0,1	1290,32	201,43	0,62	2,10	174,25	10,40
KOA 0,1	775,40	448,31	0,31	2,10	203,61	13,65
ASA 0,2	1282,34	378,13	1,53	1,04	105,26	9,98
KAA 0,2	1304,52	45,25	1,35	5,30	65,63	11,60
AKA 0,2	765,41	442,55	0,71	1,04	163,83	11,70
KOA 0,2	1131,02	98,09	0,79	6,90	97,33	14,54

Kalmakhanova *et al.* (2019), reports in their study the heavy metal composition of the clays used to obtain the adsorbent. Of the metals reported by the authors, Cu is common with this study. However, this metal was not identified in the adsorbents.

It is observed that in three of the tested samples, there is an increase in the concentration of this metal, although the values are well below the established limit.

Except nickel and chromium, the other metals analyzed have values within the limits allowed by the legislation, as indicated in Table 25. Although they are imprecise values among them.

There are some justifications, as previously explained in the tests with activated carbon, for the results that do not have coherence between them. In the case of tests with clays, the equipment reading signal is the main source of imprecision because the values of some heavy metals in the samples are smaller than the first point of the calibration curve used for the measurements and in the case of nickel, values above the maximum of the calibration curve. Thus, values of these heavy metals were measured, above the limit of detection, but these values are not within the limit of quantification of the equipment used.

6. Proposal for the leachate treatment system

The analyzed parameters show that for this leachate under study to be used as Fertilizer and classified specifically as a liquid organomineral fertilizer, according to the Regulation of the Parliament and Municipality (2019), it is necessary a slight water removal from the effluent, so that it exhibits at least 3% TOC. It is also necessary to remove the nickel and chromium metals, since they are above the limits allowed by legislation. Additionally, the leachate must possess enough potassium for this classification, because as it can be observed from the presented results, the contents of nitrogen and phosphorus were not enough.

Therefore, it is emphasized that for the treatment to be effective for the desired purpose, it is important to choose the treatment process efficiently. Physico-chemical processes are recommended for the removal of inorganic pollutants, heavy metals and oils and greases (Oliveira Junior, 2013). In this case it is not indicated that there is biological treatment, because it would cause organic matter removal, and having in mind the goal of using this final product, it is important that this organic content remains.

Knowing that the storage tank of this liquid waste in the Company Resíduos do Nordeste, EIM, receives all the effluent without any type of separation, that is, it has coarse material in its composition, it is suggested the implementation of grids as a preliminary treatment, where the effluent passes through coarse grids to remove large solids.

After the grids, there must be an equalization tank, the effluent will enter a large tank, from which it is pumped to the treatment line, this process allows to control the flow rates in the system, to avoid variations in the organic load, to control the pH of the effluent, which must be kept close to the neutral so as not to alter the soil characteristics in which it will be applied. The equalization tank also serves to keep the leachate homogeneous within that space, maintaining the same characteristics at any point.

Next, the filtration process, which is a mechanical method of separation, is indicated, with the main objective being the removal of suspended solids. This method consists of forcing the solution stream through a porous structure, the filter, which will retain particles of larger dimensions than the pores. It is noteworthy that analyzes of the

same parameters were performed, after filtration of the leachate, in a laboratory scale. It is suggested to use a filter press for this purpose.

The use of unitary operations such as chemical precipitation or coagulation/flocculation is not recommended, since phosphorus and organic matter present in the suspension may be eliminated, respectively, which would impair the required concentration of these components in the composition of the liquid organomineral fertilizer.

It is then necessary to perform the concentration of the leachate so that it reaches the TOC content required to be used as fertilizer. The concentration should be performed with the minimum factor of at least 1,19 times the original. There are some options for carrying out this process, such as evaporation or reverse osmosis.

To carry out the evaporation of this effluent, it would be necessary a high energy expenditure, which could not be economically viable for the company. With the development of membrane separation processes where the removal of water from the effluent does not require phase transfer it has become economically viable to use this process to concentrate solutions. Reverse osmosis is a very viable option as it separates and concentrates the compounds without modifying their molecular form. In addition, the membrane process requires less energy than other alternatives because there is no phase change, the equipment is compact and could operate continuously (Rosa, 2014).

It is important to consider the economic viability of these two concentration systems and the concentration factor achieved for each process, so that the best option chosen in this step is chosen.

For the removal of heavy metals, the ion exchange process is suggested.

Jimenez *et al.* (2004), tested the natural zeolite in this process, and pointed out that the mineral has a high adsorbent power for the removal of cadmium, chromium, manganese and nickel metals.

According to the authors, the tests indicated that there was no change in the concentration of the solutions in the absence of the adsorbent. They stated that the amount of solute adsorbed at a constant temperature increases with the concentration of the solution. In the tests performed, the authors verified a total removal of chromium in

concentrations up to 50 mg/L, and reaching 96,5% retention when the effluent contained 100 mg/L of chromium. The retention of cadmium, nickel and manganese was also practically total at low concentrations and reached about 75% with 50 mg/L of each metal.

The solids that will be removed throughout the treatment process should be sent to the landfill, which is in the same plant where would be implemented the treatment plant for the recovery of the leachate in liquid fertilizer.

After the treatment and application of the leachate in legislation, the final product must be transported, stored and marketed, following the recommendations of the Regulation of the European parliament and the municipality (2019).

Figure 20 shows the suggested treatment scheme to meet the standards required by legislation for liquid organomineral fertilizers.

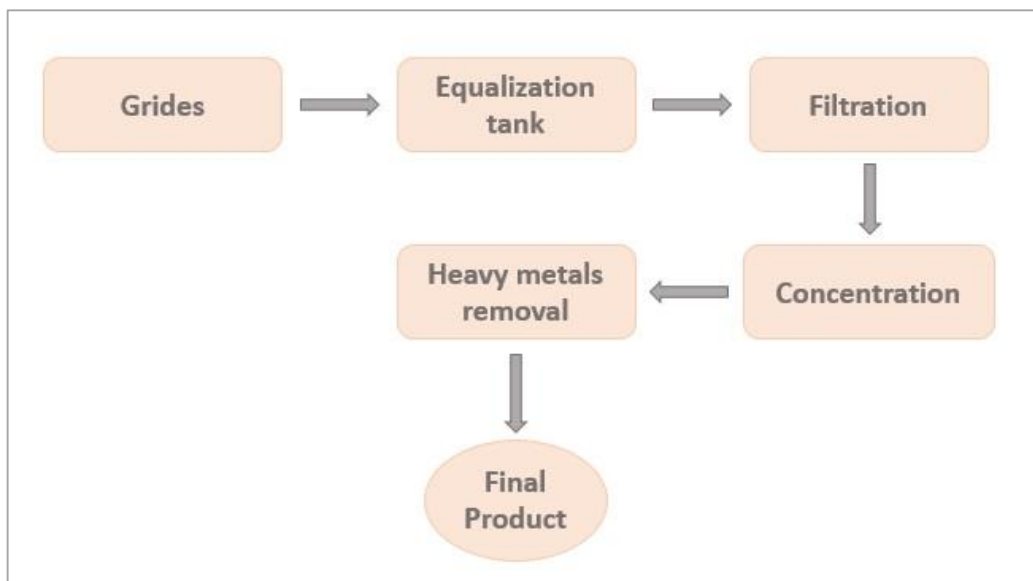


Figure 20. Suggested treatment scheme for leachate recovery in liquid organomineral fertilizer.

7. Conclusions

Faced with the adversities encountered for the most adequate final destination of waste, research and studies are essential to propose alternatives that can be performed in order to transform waste into products, attributing monetary value to that previously to a treatment, was considered a problem.

This study presented the characterization of a leachate obtained through a recovery line from the company Resíduos do Nordeste, EIM, so that the obtained data could be compared to the current legislation, in order to use this slurry as a liquid fertilizer, in this way, with the characterization, an effluent treatment system has been proposed so that this leachate can be used in the future as fertilizer liquid organomineral, following the standards required by the Regulation of the European Parliament and of the Council (2019).

With the analysis of total organic carbon, it was observed that the concentration of at least 1,19× of the original leachate is necessary, so that the required minimum content is reached, i.e. 3% of TOC. It was also observed a dependence of the density on the TOC content, the higher the percentage of total organic carbon present in the sample, the greater the density of the leachate. This correlation was proved through the Pearson coefficient, obtaining correlation in the order of $\rho = 0,998479$.

For application to the soil, it is interesting that the liquid fertilizer has pH close to the neutral, so that it does not alter soil characteristics. The Original, Filtro 03/04 and concentrated samples showed pH between 6 and 8.

The analyzes of total solids and fixed solids showed little variation for the Original and Filtro 03/04 samples, and it was observed that the fraction of organic material in these samples is higher than the inorganic fraction. The concentrated samples show slightly higher solids content due to the elimination of water. During the process of concentration of these samples, volatilization of organic components occurred, due to the heating process. In this way, it was verified that the inorganic fraction, in this case, is greater.

The concentration of phosphorus in the samples did not reach the minimum value established by the legislation, being less than 20 ppm in all samples analyzed.

Total Nitrogen, Ammoniacal and Organic Nitrogen levels were not enough to fit the leachate as an organomineral liquid fertilizer.

The Regulation of the European Parliament and the county (2019), calls for at least one of the primary nutrients to meet the established values. It is believed that the sample has Potassium content higher than the minimum required, however, it has not been possible to perform this analysis so far.

With the quantification of heavy metals, Zinc, Copper, Cadmium and Lead were found to be below the limit allowed by the legislation. However, it is necessary for the Nickel and Chromium metals to undergo a removal process prior to the use of the leachate as a fertilizer material.

Tests were performed with adsorbents from two different origins, produced by parallel research at the Polytechnic Institute of Bragança. Three adsorbents obtained from an organic compound were tested in the four leachate samples. The activated carbon showed that in addition to adsorbing the components, it also leaches them to the sample, which can become a difficulty for the use of this product.

Another test was carried out with four adsorbents obtained through clays, under the same previous conditions. Only the AKA sample showed to adsorb and did not leach the TOC with the increase of its mass, the other tests presented the same behavior as the activated carbon.

It is believed to be possible the valorization of the studied leachate, however, complementary analyzes are necessary for a complete classification as liquid organomineral fertilizer. In addition to an economic feasibility analysis for the implementation of the proposed treatment system.

8. Suggestions for future work

For completeness and success of this project, there are some considerations to be made for future work.

It is necessary to rework the heavy metals analyzes for all the samples and to carry out the analyzes for the Hg, As and Biuret, which could not be carried out so far, in order to know the exact concentration of the metals present in the leachate. It is also necessary to carry out the analyzes of the Potassium content for the Original, Filtro 03/04, 1,19× and 1,85× samples, with the objective of confirming the classification of the material as a liquid organomineral fertilizer.

The microbiological analysis must be carried out in order to comply with the Regulation of the European Parliament and of the Council (2019).

After completing the work with these analyzes, it is suggested that other types of adsorbent materials, such as the aforementioned zeolites, be tested for the efficient removal of heavy metals.

Another work that would make great contribution to this line of study would be the laboratory-scale test of the product submitted to the suggested treatments, i.e. the test of the application of the liquid organomineral fertilizer to cultivable soils.

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