ROGÉRIO MACHADO PINTO FARAGE

APLICAÇÃO DOS SUB-PRODUTOS ALCALINOS DA INDÚSTRIA DE POLPA CELULÓSICA KRAFT EM ATERROS SANITÁRIOS E NA REMEDIAÇÃO DE DRENAGEM ÁCIDA

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Ciência Florestal, para obtenção do título de *Doctor Scientiae*.

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APROVADA: 21 de setembro de 2018.

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(Coorientador)

Cláudio Mudadu Silva
(Orientador)

Dedico este intervalo no tempo aos meus pais (Binguim e Filhota), meus irmãos (Pirulito e Magro) e minha irmã (Minina). Vocês são minha luz nesse mundo louco.

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À FIBRIA (Brasil) à CELBI (Portugal).

BIOGRAFIA

Rogério Machado Pinto Farage, filho de Geraldo Pinto Farage e Maria da Conceição Machado Pinto Farage, nasceu em 15/11/1974 na cidade de Cataguases, Minas Gerais. Graduou-se em Adminstração de Empresas em 1999, pela Faculdade de Ciências Contábeis e Administrativas Machado Sobrinho, trabalhando como Analista de Compras na Cia Força e Luz Cataguases-Leopoldina, hoje Grupo ENERGISA. Especializou-se em Gestão de Negócios e Empreendimentos em 2002, pela Universidade Federal de Juiz de Fora. Formou-se em Técnico em Meio Ambiente em 2007, pelo Centro Federal de Educação Tecnológica – CEFET de Rio Pomba-MG. Obteve o título de Mestre em Engenharia Ambiental em 2009, pela Universidade Federal de Ouro Preto. Atua desde 2009 na área ambiental como consultor, com ênfase em gestão e regularização ambiental de indústrias, diagnóstico e planos de controle ambiental na indústria e gerenciamento de resíduos sólidos. Neste intervalo foi sócio-fundador da empresa de consultoria SIMBIOSE AMBIENTAL, desenvolvendo trabalhos em parceria com os setores público e privado, com destaque ao Sindicato do Polo Moveleiro de Ubá, SEBRAE e FIEMG. Atuou ainda como docente em cursos técnicos, de pós-graduação e graduação. Com o ingresso no Programa de Doutorado, do Departamento de Engenharia Florestal da Universidade Federal de Viçosa, em 2014, trabalhou com pesquisa e monitoramento em estações de tratamento de efluentes industriais. Neste intervalo, trabalhou ainda como voluntário no Projeto Semear Atitude, idealizado pela Engenheira de Alimentos Luisa de Oliveira Mendonça, com objetivo de despertar o conhecimento e consciência ambiental, assim como boas práticas de alimentação, em crianças do ensino básico em escolas públicas. Foi pesquisador junto ao Departamento de Engenharia Química da Universidade de Coimbra, Portugal, de março a julho/2018, pelo Programa “be a Doc”. Na área cultural é instrumentista, com domínio intermediário de harmônicas diatônicas, preferencialmente nos estilos rock e blues, apresentando-se em festivais como Ibitipocablues, VIJAZZ e festival regional de viola de Piacatuba-MG, além da participação na gravação do 1° álbum da banda StoneAge e no videoclipe da banda Couro de Cascavel, financiado pela Fábrica do Futuro.

SUMÁRIO

RESUMO

FARAGE, Rogério Machado Pinto, D.Sc., Universidade Federal de Viçosa, setembro de 2018. **Aplicação dos sub-produtos alcalinos da indústria de polpa celulósica kraft em aterros sanitários e na remediação de drenagem ácida**. Orientador: Cláudio Mudadu Silva. Coorientadores: José João Lelis Leal de Souza e Ana Augusta Passos Rezende.

Motivado pela necessidade de material para cobertura intermediária em aterros sanitários, pela busca por materiais em quantidade e custos acessíveis para uso como barreira reativa permeável (BRP) no tratamento/remediação de drenagem ácida de mineração e redução dos custos das fábricas de polpa kraft com o tratamento e disposição final dos resíduos alcalinos dregs, grits e lama de cal, o presente estudo objetivou avaliar o uso destes resíduos alcalinos para estas aplicações sob a variável ambiental. Baseado nos procedimentos operacionais para aterros sanitários no Brasil, a demanda de material para cobertura intermediária é de cerca de 17 milhões m³/ano, consumindo todo o volume dos resíduos alcalinos gerados pelo setor de polpa kraft no Brasil (cerca de 380 mil t/ano), com uma redução de custos de R$ 30 milhões / ano para as fábricas. Quanto ao tratamento das drenagens ácidas do setor de mineração, os sistemas de tratamento *in loco*, com destaque ao uso de BRP, representam uma opção mais atrativa devido aos reduzidos custos de instalação e manutenção, quando comparados aos sistemas ativos, que consistem na construção de estações de tratamento de efluentes e sistemas de bombeamento. As BRP's são instaladas no fluxo das drenagens ácidas, atuando na retenção de contaminantes, a exemplo de metais e sulfatos, através de mecanismos como adsorção, troca iônica e precipitação. A vida útil dos materiais adsorventes implica na opção por materiais de baixo custo e elevada disponibilidade, motivando estudos sobre o reuso de resíduos industriais. O presente estudo avaliou as possíveis restrições de uso dos materiais em aterros sanitários, notamente sobre a ação dos microrganismos responsáveis pela estabilização da fração orgânica dos resíduos no interior dos aterros e posteriormente no tratamento do chorume. Avaliou-se ainda a remoção de metais no chorume gerado em aterros sanitários quando da utilização de um composto de dregs+grits e lama de cal. Finalmente, estudou-se a capacidade de remoção de cobre e sulfato em drenagem ácida de mineração com o uso de dregs e grits. O uso do composto dregs+grits e da lama de cal como cobertura intermediária em aterros sanitários foi dividido em três etapas: construção e enchimento de 3 aterros sanitários experimentais, sendo um controle (sem uso dos resíduos alcalinos), monitorados durante 6 meses através dos respectivos chorumes gerados; tratamento biológico dos chorumes gerados nas unidades experimentais com cobertura de dregs+grits e da controle (sem cobertura intermediária), por meio de reatores aeróbios; construção de 9 colunas preenchidas com o composto de dregs+grits (3 colunas), com lama de cal (3 colunas) e com solo (3 colunas), seguido da aplicação periódica de uma solução de chorume e metais (Cd, Cr, Cu, Mn, Ni e Pb). Os valores de DQO dos chorumes gerados na unidade experimental com cobertura de lama de cal e para a unidade controle foram similares, 2.800 mg/L e 3.300 mg/L, respectivamente, ao final do intervalo de monitoramento. O chorume da unidade experimental com cobertura do composto de dregs+grits manteve DQO de 32.000 mg/L neste intervalo, diminuindo para 2.800 mg/L após 9 meses, enquanto os chorumes da unidade com lama de cal e da controle passaram a 800 mg/L e 1.300 mg/L, respectivamente. Este comportamento sugere a presença de agente inibidor das atividades da microbiota na unidade com dregs+grits, a exemplo do sódio, com concentração 13 vezes maior que no chorume da unidade controle. A eficiência média na remoção de DQO através do tratamento biológico dos chorumes gerados nas unidades experimentais com cobertura do composto de dregs+grits e da controle foram similares, entre 70% e 90%. As retenções de metais nos ensaios de coluna foram similares para a lama de cal e solo, acima de 70%, com oscilação para o Cu durante os intervalos das aplicações nas colunas com lama de cal. As colunas com dregs apresentaram dessorção de Cu e comportamento oscilatório nas retenções de Cd, Cr e Ni ao longo do monitoramento das colunas. A remoção de Cu e sulfato em drenagem ácida de mineração foi avaliada através de ensaios de cinética de adsorção, ensaios em batelada com diferentes relações S:L (adsorvente: adsorvato) e ensaios em coluna. A retenção de Cu, em ambiente alcalino, foi similar para dregs e grits, superior a 99% para relação S:L de 1:10, sugerindo mecanismo de precipitação. A remoção de sulfato foi superior a 70% com o uso de ambos materiais, em ambiente ácido (pH <5).

ABSTRACT

FARAGE, Rogério Machado Pinto, D.Sc., Universidade Federal de Viçosa, September, 2018. **Application of the alkaline by-products from kraft pulp industry in landfills and acid drainage remediation.** Advisor: Cláudio Mudadu Silva. Co-advisors: José João Lelis Leal de Souza and Ana Augusta Passos Rezende.

Motivated by demand for intermediate covering material in landfills, by search for alternative materials that be use as permeable reactive barries for acid mine drainage treatment and to eliminate or reduce the costs with final disposal of the alkaline wastes dregs, grits and lime mud generates in pulp kraft mills, the present study evaluated the use of this alkaline wastes in this applications under the environmental variable. Based on operation procedures for landfills in Brazil, the consumption of intermediate covering material is 17 million m³/year. The alkaline wastes (dregs, grits and lime mud) generated by pulp kraft mill in Brazil, represents 5% this volume (380,000 t/year), with an approximate cost of US$ 7.5 millions for final disposal. In the acid mine drainage treatments the permeable reactive barrier (PRB) is commoly adopted due lower costs with installation and monitoring, compared to pumping systems and treatment plants. The PRB are installed in the acid mine drainage flow, like a filter, retaining contaminants such as metals and sulfate through mechanisms as adsorption, ion change and chemical precipitation. The waste industries reuse is motivated like PRB due to the time life of the materials, being necessary search about materials with low costs and high disponibility. The study evaluated the possible restrictions of the use of the materials in landfills, especially on the action of the microorganisms responsible for stabilizing the organic fraction of the residues within the landfills and on the treatment of the leachate. It was also evaluated the potential for the removal of metals in the leachate generated in landfills when dregs+grits were used as intermediate covering. Copper and sulphate removal in the acid drainage of mines were evaluated using dregs and grits as PRB fillers. The use of dregs+grits and lime mud as intermediate covering in sanitary landfills was studied in three stages: building and filling of 3 experimental sanitary landfills, being U1 (intermediate covering of dregs+grits), U2 (intermediate covering of lime mud) and U3 (without intermediate covering). It was monitored during 6 months through the leachates; biologic treatment of the leachates from experimental sanitary landfills, using aerobical reactores; filling of 9 columns with dregs+grits (3 columns), lime mud (3 columns) and soil (3 columns), with periodic application of leachate and metals solution (Cd, Cr, Cu, Mn, Ni and Pb). The COD of the leachates from U2 and U3 were similares, 2,800 mg/L and 3,300 mg/L, respectively, at the end of the monitoring interval. The COD of the leachate from U1 remained 32,000 mg/L in the same interval, decreasing for 2,800 mg/L after 9 months, while the leachate from U2 and

U3 decreased for 800 mg/L and 1,300 mg/L, respectively. This behavior suggests presence of inhibitory agent, such as sodium, with concentration 13 times higher than the leachate from U3 (control unit). The average efficiency on COD removal of the leachates from U1 and U3, through of the aerobic biologic treatment were similar, between 70% and 90%. The metals retention in the column assays were similares for lime mud and soil, above 70%, oscillating for the Cu during the applications on the lime mud columns. The columns filled with dregs+grits presented Cu dessorption and oscillatory behavior in the Cd, Cr and Ni retention throughout of the columns monitoring. The Cu and sulfate removal in acid mine drainage was evaluated through of adsorption kinetics assays, batch test with differents S:L (adsorbent: adsorbate) rates and column test. The Cu retention was above 99% for dregs and grits, in alkaline conditions, for S:L rate of 1:10, suggesting precipitation mechanism. The sulfate removal was above 70% using both materials, in acid conditions (pH < 5).

INTRODUÇÃO GERAL

O procedimento operacional em aterros sanitários de resíduos sólidos urbanos (RSU) requer cobertura intermediária para o controle de aspectos ambientais, como o transporte de resíduos pelo vento, a emissão de gases, os odores e a presença de vetores, consumindo cerca de 17 milhões de metros cúbicos de material por ano (ABRELPE, 2015). O solo é comumente usado como material de cobertura intermediária e apresenta vantagens como o baixo custo e o potencial para sorção de metais ([1]Bellir et al., 2005). Contudo, a extração de solo degrada as áreas de empréstimo, justificando a busca de materiais alternativos.

O chorume, importante aspecto ambiental em aterros sanitários, caracteriza-se por um líquido de cor escura, formado pela água da chuva e umidade dos resíduos. As características físicas, químicas e biológicas, como compostos xenobióticos orgânicos, alta carga orgânica, macro-compostos inorgânicos e metais podem variar ao longo do tempo. O volume de chorumes em aterros sanitários depende notadamente das condições meteorológicas locais, idade e natureza dos resíduos, e operação do aterro ([2]Chrıstensen et al., 1996).

Na indústria de polpa celulósica kraft, a separação da fibra é feita a alta temperatura e pressão, em meio alcalino (licor branco), pela adição de hidróxido de sódio e sulfeto de sódio. O licor negro, subproduto desse processo, consiste principalmente de lignina e outras substâncias orgânicas, como extrativos e hemicelulose, e compostos inorgânicos de sódio e enxofre, sendo queimado na na caldeira de recuperação com reaproveitamento energético. Os fundidos são retirados da caldeira e enviados para o processo de dissolução, clarificação e caustificação. Nesse processo de recuperação do licor, são gerados três resíduos de caráter alcalino: dregs, grits e lama de cal, sendo geralmente dispostos em aterros sanitários e/ou industriais ([3]Makitalo et al., 2014).

O uso de dregs, grits e lama de cal como material de cobertura intermediário para aterros sanitários urbanos poderia ser uma solução ambiental interessante para a indústria e para os municípios. As indústrias reduziriam seus custos com tratamento e/ou disposição final, eliminando ou diminuindo seus passivos ambientais pelo retorno destes resíduos à cadeia produtiva na forma de material de cobertura em aterros. Haveria ainda ganhos

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[1] Bellir, K. et al., 2005. Study of retention of metals by natural material used as liners in landfills. Desalination 185, 111 – 119.

[2] Chrıstensen, J. B. Et al., 1996. Efect of dissolved organic carbon on the mobility of cadmium, nickel and zinc in leachate polluted groundwater. Water Research 30, n. 12, 3037 – 3049.

[3] Makıtalo, M. et al., 2014. Characterization of green liquor dregs, potentially useful for prevention of the formation of acid rock drainage. Minerals 4, 330 – 344.

ambientais e sanitários nos aterros sanitários dos municípios vizinhos e adjacentes, pela redução restringindo a extração de solo que resulta na degradação de novas áreas, diminuindo a incidência de vetores nos aterros devido a alcalinidade dos materiais em estudo, além do potencial de retenção e redução dos níveis de metais nos chorumes, notadamente pelo mecanismo de precipitação química favorecido pela alcalinidade dos materiais em estudo, contribuindo para a melhoria nas condições do tratamento biológico do chorume. Não obstante, faz-se necessária a avaliação de três importantes aspectos no uso de dregs, grits e lama de cal nos aterros sanitários urbanos: i) comportamento da atividade biológica na célula do aterro; ii) a qualidade do chorume gerado e sua biotratabilidade; iii) a potencial retenção de metais no chorume.

Esse trabalho objetivou identificar os benefícios e/ou restrições ao uso do composto de dregs + grits e lama de cal como cobertura intermediária em aterros sanitários, em substituição ao solo. O estudo foi dividido em quatro fases que equivalem a cada capítulo dessa tese.

Capitulo 1 - Na Fase 1 foram construídos 3 unidades experimentais de aterramento de resíduos sólidos urbanos – RSU, preenchidas com resíduos coletados no município de Viçosa, Minas Gerais, e coberturas intermediárias, intercaladas aos resíduos, formadas por dregs + grits (unidade 1), lama de cal (unidade 2) e solo (unidade 3). Estas unidades foram monitoradas durante 6 meses, mediante a amostragem semanal do chorume gerado, permitindo avaliar a influência destes materiais sobre a atividade microbiológica, responsável pela estabilização da fração orgânica da massa de resíduos.

Capitulo 2 - Durante a Fase 2 foram construídos 3 reatores biológicos aeróbios para o tratamento dos chorumes coletados nas três unidades experimentais. O principal parâmetro de monitoramento foi a demanda química de oxigênio – DQO, através do qual se determina, de forma indireta, a estabilização da matéria orgânica presente nos chorumes. O monitoramento foi realizado em três etapas, com diferentes relações entre alimento e microrganismos (A/M), objetivando estabelecer a relação ótima.

Capitulo 3 - Na Fase 3, avaliou-se a capacidade de retenção de metais pelo composto de dregs + grits e da lama de cal através da construção e monitoramento de 9 colunas preenchidas com dregs + grits, lama de cal e solo, três para cada material adsorvente. Foram feitas 18 aplicações de uma solução de chorume e metais (Cd, Cr, Cu, Mn, Ni e Pb), totalizando um volume percolado de 1.440 mL por coluna. A identificação do ponto de saturação dos materiais adsorventes permite determinar a relação ótima entre adsorvente e adsorvato.

Capítulo 4 - Nesta fase foi avaliado o uso de dregs e grits como material de preenchimento em barreiras reativas permeáveis para remoção de cobre e sulfato em drenagens ácidas de minas, resultado de um intervalo de 4 meses de mobilidade junto ao Departamento de Engenharia Química da Universidade de Coimbra. Este estudo foi motivado sob dois aspectos: pela demanda apresentada pelo setor de polpa celulósica em Portugal, objetivando redução dos custos com tratamento e disposição final destes resíduos, através da sua reinserção baseado na teoria da Economia Circular, mecanismo amplamente discutido entre os países da União Européia. Além disso, o importante setor de mineração deste país demanda tecnologias cada vez mais sustentáveis e econômicas para remediação da drenagem ácida, aspecto ambiental intrínseco às suas atividades.

Capítulo 1

Intermediate covering of municipal sanitary landfills with alkaline by-products of grits, dregs and lime mud from kraft pulp production

ABSTRACT

The increasing demand for intermediate covering materials in municipal sanitary landfills stimulates the study for the finding of alternative materials for this purpose. This study evaluates the use of dregs, grits and lime mud generated in pulp kraft mills in considerably large volumes as covering materials in urban sanitary landfill. Emphasis were given on the generated leachate quality and effects on the microbiological activities within the cells. Three experimental units simulating landfill cells with 3 m high and 1 m diameter were assembled, and monitored during 6 months. Unit U1 was filled with municipal solid waste (MSW) and used as covering material a mixture of dregs and grits in a proportion of 70% and 30%, respectively. Unit U2 used lime mud as covering material and Unit U3 was filled solely with MSW without any covering material (control). The leachate COD concentration decreased to 91% and 92%, respectively, for U2 and U3, decrease not observed for U1, which remained above 30,000 mg / L, to the end of the monitoring interval. 9 months after this interval, the COD decrease on U1, U2 and U3 were 92%, 98% and 97%, respectively. The metal concentrations in the leachates of the three experimental units were below the legal limits for discharge into watercourses in Brazil. The substitution of soil by the mixture of dregs and grits, and lime mud showed to be technically feasible, but the concentration of sodium in the leachate produced in the Unit U1 (12,480 mg/L) was 13 times higher than U3 (control unit) and should be taken into consideration. This fact could have caused inhibition of the bioactivity in the cell and delayed the organic matter degradation.

Keywords: landfill, leachate, metals, waste solid, by-products, reuse

1. INTRODUCTION

Around 78.5 million tons per year of municipal solid waste (MSW) are generated in Brazil and 60% are disposal in sanitary landfills (ABRELPE, 2017).

The generation of leachate and the gas emissions are the main environmental aspects in MSW landfills. Physical, chemical and biological characteristics of the leachate, a dark colored liquid formed by rain water, stabilization of the organic matter and leaching of the residues in the cells of the landills (Yahmed et al., 2009; Alkalay et al., 1998; Bhatt et al., 2017) can vary with age, amount of water incorporated and composition of the solid (Kheradmand et al., 2010). Organic xenobiotic compounds, high organic load, inorganic macrocompounds and metals are the potential contaminants in the leachates (Chrıstensen et al., 1996; Nagashima et al., 2009) and should be kept below the environmental regulation limits for its discharge into watercourses (Nagashima et al., 2009). Flow rates between 25 and 280 m^3/d of leachate were identified in landfills in Germany (Mohammad et al., 2017) and 26,000 m^3/year in Jebel Chekir, Tunisia (Yahmed et al., 2009), respectively.

The National Solid Waste Policy in Brazil legislates the final disposal of MSW in landfills according to an operational procedure standardized by the Brazilian Association of Technical Standards (ABNT), recommends the intermediate covering of MSW in sanitary landfills to control environmental aspects such as the transport of waste by wind, gas emission, odors and the presence of vectors, consuming about 17 million cubic meters of material per year (ABRELPE, 2017).

Soil is the most commonly used material as a landfill cover for MSW in Brazil, presenting advantages such as low cost and potential for metal sorption (Bellir et al., 2005). Soil extraction however, degrades areas, justifying the search for alternative materials to reduce this impact. Sanitary sludge, building material waste and boiler ash (Travar et al., 2015) have been investigated as intermediate coverage of MSW in sanitary landfills.

Materials used for final landfill coverage should have low permeability, minimizing the inflow of rain water, reducing the production of leachate and subsequently reducing treatment costs. On the other hand, low permeability intermediate coverings, in the presence of municipal solid waste (MSW) that has 70% of organic material and 72% of moisture content (Chian, 1977) can accumulate water and leachate along the landfill profile, leading to a breakdown of the landfill embankment and cause material transport and contamination of adjacent areas. Moreover, low moisture into landfill, due an impermeable covering, can reduce the efficiency the organic material degradation process and makes unfeasible leachate recirculation techniques (Reinhart and Al-Yousfi, 1996).

In Brazil, the solid wastes generators, such as the pulp industry, are responsible for the management and final disposal of their solid wastes. Dregs, grits and lime mud, characterized for being alkaline by-products with pH between 10 and 12 (Martıns et al., 2007; Poykio et al., 2006) and generated in the process of black liquor chemical recovery in the kraft pulp process, are usually disposed of in industrial landfills, such as in Sweden, where 240,000 t/year dregs are generated (Makitalo et al., 2014). About 341,000 tons of dregs and grits are generated per year in Brazil (Siqueira and Holanda, 2013). Lime mud generation from kraft pulp production is estimated to be 6% and is withdrawn during plant shutdowns for maintenance of lime kilns (Sthiannopkao and Sreesai, 2009).

The aim of this study was to evaluate the use of dregs, grits and lime mud generated in pulp kraft mills as covering materials in urban sanitary landfill. Emphasis were given on the generated leachate quality and effects on the microbiological activities within the cells.

2. METHODS

2.1. Experimental setup

Three experimental units (3 m high and 1 m diameter each) were built simulating a sanitary landfill cell. A PVC pipe was installed at the base, filled with 20 cm of gravel, for drainage and leachate collection (Figure 1). The Unit U1 was filled with material composed of dregs and grits (70% dregs and 30% grits) and MSW. The Unit U2 was filled with MSW and lime mud as intermediate covering. Unit U3 (control) was filled up with only MSW, without intermediate covering. These units were filled with a layer of gravel at the base and soil on the top. Plastic covers installed on the top of the three experimental units aimed to prevent rainwater entrance.

Water was introduced using plastic watering cans at pre-determined intervals and volumes (Table 3) simulating the average precipitation of the municipality of Vicosa, Minas Gerais, Brazil.

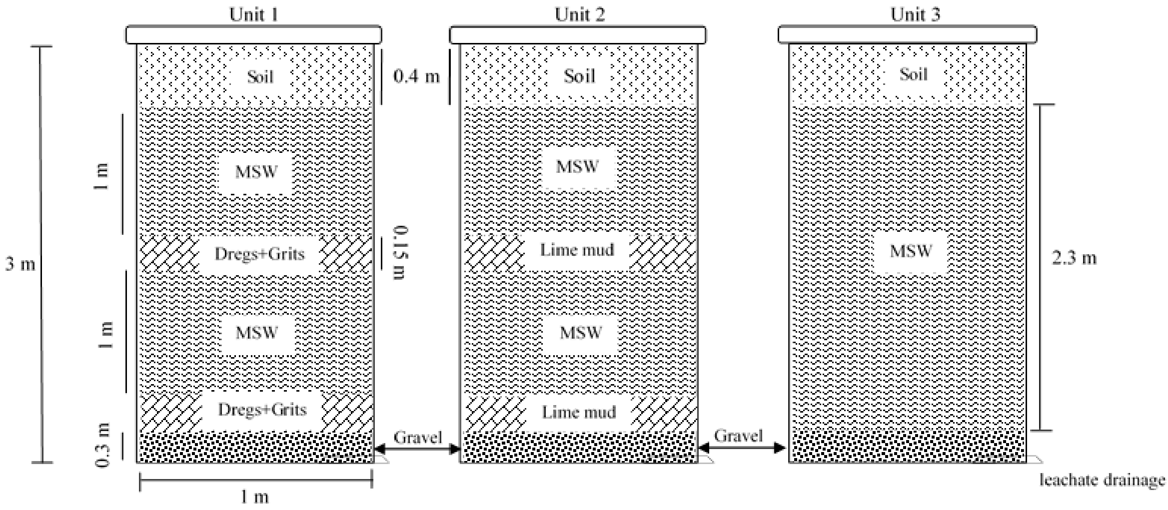

Figure 1. Experimental units of MSW

The MSW used to fill the experimental units were collected in a sanitary landfill of the city of Vicosa. The MSW (1,200 L) were homogenized on two plastic sheets (4 m x 10 m) to determine their gravimetric composition by a specific technique that divides the amount of material into four equal parts by selecting the exposed diagonals (Table 1).

Table 1. The gravimetric composition of the MSW used in the experimental

Unit	Organic matter	Plastic	Paper	Iron/Steel	Fabric	Tetra Park	Total
kg	64.0	39.0	10.0	2.0	3.5	3.5	122.0
%	52.5	32.0	8.0	1.5	3.0	3.0	100.0

The three units were filled with the same composition as the MSW, varying the layout and volume of the materials used (Table 2). The filler material of the experimental units was not compacted and a 40 cm soil layer (Cambisol) was applied on the top of the three units. The filling sequence of the units was gravel, alkaline by-products and alternating MSW and soil (Figure 2).

Table 2. Profiles of the experimental units filled with material composed of dregs and grits and MSW (U1), lime mud and MSW (U2) and control with MSW (U3)

Profiles	Height (m)	U1	U2	U3
1	0.40	Soil	Soil	Soil
2	1.00	MSW	MSW	MSW
3	0.15	*Grits and Dregs*	Lime mud	MSW
4	1.00	MSW	MSW	MSW
5	0.15	*Grits and Dregs*	Lime mud	MSW
6	0.30	Gravel	Gravel	Gravel

Figure 2. Filling the experimental unit U1 (*grits and dregs* and MSW)

The rain simulation in the experimental units carried out once time per week, totaling 630 L in six months. The water balance was calculated by the difference between the volumes of applied water in each unit and the percolated water collected at the bottom of each cell.

2.2. Physical-chemical characterization of the covering materials (dregs, grits and lime mud)

The chemical characterization of the alkaline by-products (dregs, grits and lime mud) used in the experiments is showed in Table 3 and was determined by X-Ray Dispersive Energy Spectrometry (EDX) using a SHIMADZU EDX 1300 micro model spectrometer. The mixture of dregs and grits is composed of 70% dregs and 30% grits by volume.

Table 3. Metal and metalloid content (%) in dregs (Dr), grits (Gr) and lime mud (LM) used to fill the experimental units

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SiO_2	P_2O_5	CO_3	Cl	SO_3
Dr	0.46	33.17	1.24	0.49	1.99	2.36	4.09	0.02	49.38	0.22	3.72
Gr	0.22	53.65	0.64	0.35	0.50	2.13	3.93	0.03	34.28	0.19	0.71
LM	0.07	57.12	0.20	0.26	0.91	2.32	3.58	0.03	31.36	0.14	0.40

2.3. Physical-chemical parameters

Electrical conductivity (EC), Chemical Oxygen Demand (COD), pH, sodium, nitrogen, phosphorus, total solids and metals (Cd, Cr, Cu, Ni, Pb and Zn) in the leachates were analyzed following the Standard Methods for the Examination of Water and Wastewater (APHA, 2012) during six months. The COD was monitored between May/2015 and October/2015. Were collected 4 samples, one per week, on the 1st and 2nd months. From 3rd to 6th months was collected 1 sample to each 15 days, totalizing 16 samples. After this interval, the leachate was collected and analyzed a sample in July 2016. Sodium was determined by atomic absorption spectrophotometry according to SM – 3500 – Na B (APHA, 2012).

The total and soluble metals (Cr, Cu, Ni, Cd, Pb, Zn) were analyzed according to Standard Methods – SM 3111B and 3111D (APHA, 2012) and their concentrations determined by atomic absorption spectrophotometry.

3. RESULTS AND DISCUSSION

3.1. Water balance

The water balance of Unit U1 was similar to that of the control (Unit U3) at the end of the monitoring period (Figure 3). The Unit U2 started to drain the leachate 14 days after its filling and accumulated 10% more water than the others. The plastic structure and low hydraulic conductivity (10^{-8} to 10^{-9} m/s) of the dregs may have caused difficulties in the use of these products as intermediate covering in landfills (Makitalo et al. 2014; Modolo et al. 2010). Values similar to those recommended by the USEPA and European Commission for materials used as final coverage in landfills are less than 10^{-9} m/s (Musso et al., 2017). The similar drainage of the mixture of dregs and grits (Unit U1) and Unit U3 (only urban solid waste) was possibly because of the sandy characteristic of the mixture.

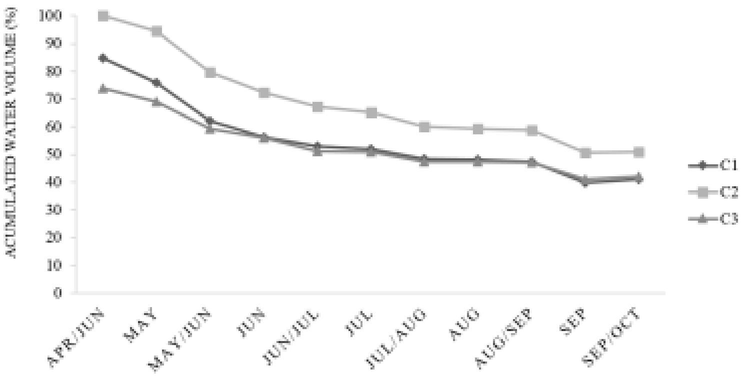

Figure 3. Hydric balance in experimental units filled with material composed of dregs and grits and MSW (U1), lime mud and MSW (U2) and control with MSW (U3)

3.2. pH, EC and COD

The pH of the leachates in units U1 and U2 were 7 to 9 during the monitoring interval, similar to the control unit (U3), which began as slightly acidic, changing to neutral or alkaline pH 40 days after the MSW was covered (Figure 4). The pH of the leachate from the control unit was within the range of 5.8 to 8.5, observed for landfills in Canada and China respectively (Renou et al. 2008) and for experimental landfills in the city of Sao Carlos, State of Sao Paulo, Brazil (Vazoller et al., 2001), from 5 to 6 and from 6 to 8, similar values suggested as ideal for the acidogenic and methanogenic phases, respectively, in anaerobic biological treatment systems (Kim et al., 2003; Ward et al., 2008; Yahmed et al., 2009). The pH ranges from 4.7 to 7.7 and from 6.3 to 8.8 were reported for the acetogenic and methanogenic phases, respectively, in Aksaray, Turkey (Alver and Altas, 2017). The stable pH of the leachates of the U1 and U2 units can be attributed to the buffering effect of the alkaline by-products, dregs and grits and lime mud (Golmaei et al., 2017; Makitalo et al., 2014). The pH variation from 4.5 to 9.0 between the acidogenic and methanogenic phases in the leachate in sanitary landfills were associated with a reduction in the ratio of BOD/COD by the stabilization of organic matter (Kjeldsen et al., 2002), from 0.7 to 0.04 (Chian and DeWalle, 1976).

The electrical conductivity (EC) of the experimental unit with MSW interspersed with dregs and grits (U1) was up to six times greater than that of the control unit (U3) at the beginning of the experiment, explained by the significant concentrations of sodium (Figure 5) in dregs and grits. EC values for the leachates from U1, U2 and U3 decreased by 58%, 41% and 56% throughout the experiment, respectively (Figure 4), possibly due to the systematic percolation of water, leaching the salts of covering materials. The electrical conductivity of units U2 and U3 (Figure 4) were similar to those of landfill leachates in southern China and Germany (Li et al., 2009; Mohammad et al., 2017) and that of Minas Leao City, Brazil, 26 mS/cm (Fleck et al., 2016). The EC is an indirect parameter for salt determination, adopted because of its practicality and speed in determining the results and its given values (Figure 4) are related to that of the sodium ion (Figure 5).

COD concentrations remained high in the leachates from U1, U2 and U3 units in the first 70 days after filling (Figure 4) and gradually decreased in units U2 and U3. The concentration of COD in the leachate of unit U1 differed from those of U2 and U3, above 30,000 mg/L until the end of monitoring (interval 16) and decreasing to values close to those of the control unit after six months of this interval. The highest leachate COD value (43,000 mg/L) observed in the control unit (U3) was within the range of 140 to 152,000 mg/L (Kjeldsen et al., 2002) and 55,000 mg/L COD in the landfill in Shiraz, Iran (Kheradmand et al. 2010). The COD curve of units U1 and U2 are in line with expectations for landfills such as anaerobic reactors (Kulikowska and Klimiuk, 2008), with an increase followed by a reduction of COD concentrations in the leachate, due to the interval for the formation of the active biomass responsible for the degradation of the organic fraction of the MSW. The initial and final values of COD in the three experimental units were similar to the two experimental landfills in São Carlos, Brazil (Vazoller et al., 2001), differing only in the interval of 300 days to obtain values below 10,000 mg/L, achieved in 120 days in the present study. The reduction of COD values in unit U1 along the intervals 16 and 17 was not monitored, making it impossible to describe their kinetics, but their behavior suggests a longer timeframe or initial resistance to the stabilization of the organic fraction of the leachate. The inhibition of the microbiological activity by the high sodium concentration, the unfavorable relationship between the demand and supply of nitrogen and phosphorus (Figure 5) and the pH, slightly alkaline at the beginning and above the values referenced in the literature (Alver and Altas, 2017; Kjeldsen et al., 2002), may be possible causes for the longer COD reduction interval in unit U1. This parameter is important for the determination of organic compounds and their monitoring is required for the discharge of wastewater into watercourses in Brazil (CONAMA, 2011). The useful life of a landfill is, on average, more than 10 years and this parameter did not show a negative impact with the use of alkaline by-products as an intermediate cover.

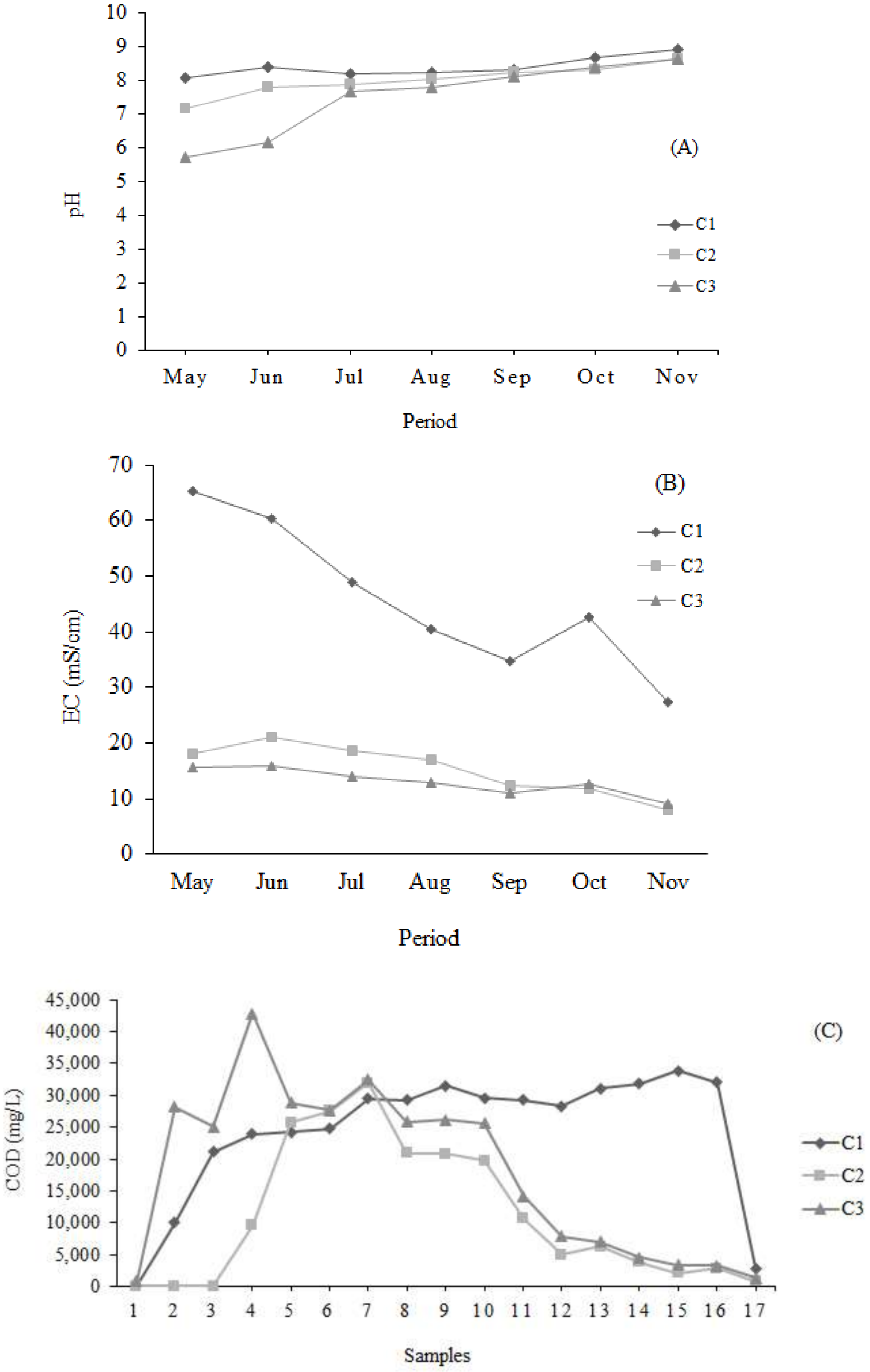

Figure 4. pH values (A), EC (B) and COD (C) in the leachate generated in the experimental units filled with composite material of dregs and grits and MSW (U1), lime sludge and MSW(U2) and control with MSW (U3)

3.3. Sodium, nitrogen and phosphorus

The values of sodium of the leachates of units U1 and U2 were 12,480 and 2,120 mg/L, respectively, higher than the control unit (U3), 870 mg/L (Figure 5). Tolerable levels of soil salinity depend on factors such as species and stage of development of plants (Cramer et al., 1994), soil permeability and climate (Banda et al., 2014), which should be considered for fertirrigation reuse of the leachates affected by the layers of dregs and grits and lime mud. The application of dregs and lime mud increased the concentrations of sodium in the soil (Pértile et al., 2012), with associated risks regarding particle dispersion and sealing (Irvine and Reid, 2001; Rengasamy and Olsson, 1991) and interference in osmotic potential (Allakhverdiev et al., 2000). Increasing Na concentrations in soils may inhibit Ca and K transport in plant roots (Cramer et al., 1994), restricting the direct application of leachate in the soil as fertirrigation, an increasingly adpoted technique (Barton et al., 2005). Total sodium values ranging from 385 to 720 mg/L in four Danish landfills (Jensen and Christensen, 1999) and from 66 to 364 mg/L in the Wysieka landfill, in Poland (Kulikowska and Klimiuk, 2008), were observed. Sodium can reduce the efficiency of treatment of leachate drained from landfills by inhibiting the metabolism of bacterial cells by the deficiency of the enzymatic action and transport of the substrates to their interior as well as causing cell lysis (Quartaroli et al., 2016). Treatment of industrial saline effluent in Tunisia and non-salt from a cannery in Egypt showed an inverse relationship between sodium concentration and COD removal efficiency in biological treatment systems (Aloui et al., 2009; Sohair et al., 2010). Metabolic activity of bacteria in wastewater with up to 100,000 mg/L of sodium (Quartaroli et al., 2016) suggests the possibility of adaptation or selection of microorganisms which may have occurred in the intervals 16 and 17 of unit U1.

The values of nitrogen (ammonia) and phosphorus in the leachate of the three experimental units, six months after filling, were from 260 to 500 mg/L and 13 to 20 mg/L respectively (Figure 5). The leachate of unit U1 presented nitrogen and phosphorus deficiency according to the ratio of 250 (COD): 5 (N): 1 (P) for anaerobic biological treatment (Metcalf and Eddy, 1991). This may have contributed to maintaining high concentrations of COD (Figure 4) in this leachate because nitrogen and phosphorus are required for the development of microorganisms (Metcalf and Eddy, 1991). The U2 and U3 units (control) presented balance or surplus between the required and available quantities of these nutrients. The concentrations of ammoniacal nitrogen ranged from 450 to 2,450 mg/L in landfill with 10 years of operation in southern China (Li et al., 2009), from 100 to 400 mg/L in landfill with a similar period of use and with a 32% organic fraction in the MSW in Wysieka, Poland (Kulikowska and Klimiuk, 2008), from 89 to 1,840 mg/L in landfills in Germany (Mohammad et al., 2017), from 36 to 820 mg/L in Denmark (Jensen and Christensen, 1999) and of 1,440 mg/L in a landfill at Minas do Leao, Brazil (Fleck et al., 2016). Ammonia nitrogen values between 500 and 1,500 mg/L are commonly found in leachates from landfills with more than three years of use and can remain within this range for long periods of time (Chu et al., 1994). Concentrations of 16.4 and 80 mg/L for total phosphorus were observed in the Borg Al Arab landfill, Egypt (El-Gohary and Kamel, 2016). Nitrogen and phosphorus, sufficient for the demand for anaerobic treatments, are usually found in MSW leachate (Alkalay et al., 1998).

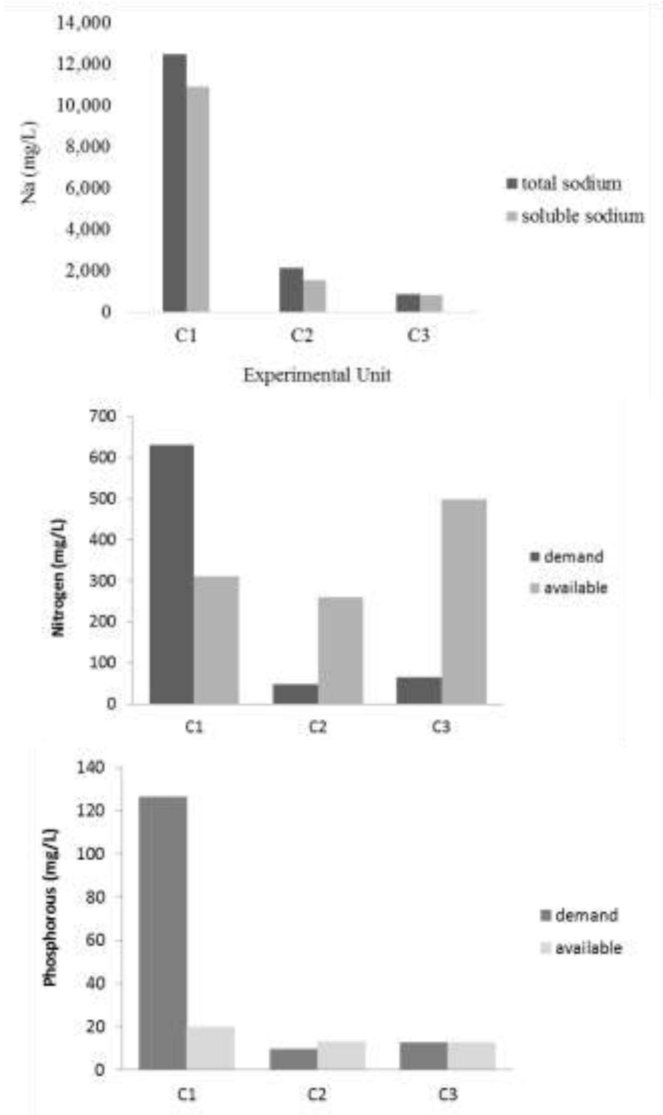

Figure 5. Sodium (A), N-ammoniacal (B) and P (C) generated in the leachate in the experimental units filled with material composed of dregs and grits and MSW (U1), lime mud and MSW (U2).

3.4. Total solids

The total solids, in the leachates of the three experimental units, varied from 8,000 mg/L (U3) to 73,000 mg/L (U1) (Figure 6), with a reduction of total fixed solids and total volatile solids in the units U2 and U3 (control). The decrease in COD concentration (Figure 4), followed by volatile solids in the same range, suggests a relationship between these parameters in units U2 and U3, differing from that observed for U1, with an increase of volatile solids and maintenance of COD concentration. This was not expected due to the inverse relationship between reaction time of the microorganisms and the concentration of organic matter and volatile suspended solids (Chian, 1997; Henry et al., 1987; Kulikowska and Klimiuk, 2008). The total solids in the leachate of unit U1 was five times greater than in the control (U3), about four times greater than the 14,900 to 17,700 mg/L of leachate from Minas do Leao, Brazil (Fleck et al., 2016) and, from the 3,160 to 7,563 mg/L of landfill leachate in Wysieka, Poland (Kulikowska and Klimiuk, 2008). The values of COD and volatile suspensed solids of leachate from two experimental units in the State of São Paulo, Brazil, decreased during the period of their use (Vazoller et al., 2001).

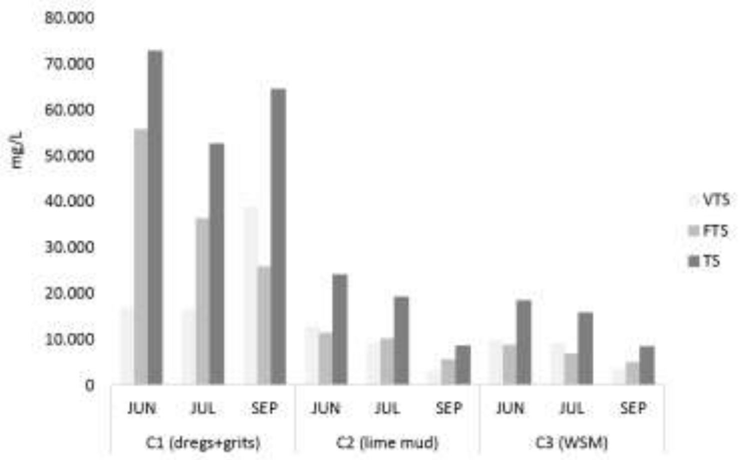

Figure 6. Concentration of total solids in the leachate generated in the experimental units filled with material composed of dregs and grits and MSW (U1), lime mud and MSW (U2) and control with MSW (U3).

3.5. Metals

The concentrations of metals (Table 4) were below detection levels (>DL) and of the maximum values recommended by the Brazilian environmental legislation for effluent discharge into watercourses (CONAMA, 2011) and lower than values for landfills in Germany (Mohammad et al., 2017). This is important because metals in leachates can inhibit the activity of the microorganisms present in the biological treatment, restrict their discharge into watercourses or make them unfeasible for fertirrigation. Values between 0.0002 and 0.004 mg/L of Cd, 0.028 and 0.084 mg/L of Ni, 0.002 and 0.034 of Cu, 0.09 and 5.3 mg of Zn, >DL and 0.19 mg/L of Cr, DL and 0.016 mg/L of Pb were found in leachate from sanitary landfills in Denmark (Jensen and Christensen, 1999). The values found were also lower than those between 0.005 and 0.003 mg/L for Cd and Ni, respectively, 3.06 mg/L for Cu, 30.5 mg/L for Zn and less than 0.004 mg/L for Cr and Pb in the landfill leachate of Aksaray, Turkey (Alver and Altas, 2017). The high buffer capacity of the dregs shows that these products can be used as an alkaline barrier for pollutants in underground plumes (Golmaei et al., 2017; Makitalo et al., 2014), contributing to sorption and precipitation mechanisms, with similar effects in landfills. Different materials, such as limestone, wood chips and volatile ash, have been studied and applied as reactive permeable barriers to neutralize pH and remove metals in acid waters from mines (Shabalala, 2013). The insoluble conditions of metals such as Cd and Al in the dregs structure after separation of the green liquor (Golmaei et al., 2017), reinforces its potential for retention of metals in leachates from landfills. The lime mud, consisting predominantly of CaO (Qin et al., 2015; Sun et al., 2013), has sorption potential of metals such as Cr (94%), Cu (99.6%) and Pb (96.8%) in wastewater (Sthiannopkao and Sreesai, 2009).

Table 4. Total concentration of crude and soluble metals in the leachate generated in the experimental units in the experimental units filled with material composed of dregs and grits and MSW (U1), lime mud and MSW (U2) and control with MSW (U3)

Elements	Unit U1		Unit U2		Unit U3		Standard Limit
	total	soluble	total	soluble	total	soluble	
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2 mg/L
Cr	0.17	0.17	0.10	<0.1	<0.1	<0.1	-
Cu	< 0.1	< 0.1	< 0.1	<0.1	<0.1	<0.1	1.0 ml/L
Ni	0.05	0.05	0.05	<0.05	<0.05	<0.05	2.0 mg/L
Pb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5 mg/L
Zn	<0.05	<0.05	<0.05	<0.05	0.13	<0.05	5.0 mg/L

4. CONCLUSIONS

The mixture of dregs and grits and the lime mud have a strong potential to replace soils as intermediate covering in sanitary landfills. However, the sodium concentration should be considered, notably because of toxicity risks associated to the microrganisms activities in the leachate biological treatment.

The similar values for COD in the leachates generated in units U1 and U2 comparatively with those of the control unit (U3) after 15 months of monitoring suggest that there is no impact of the alkaline by-products on the microorganisms responsible for the stabilization of the organic fraction of the MSW.

The risk of the accumulated metals leaching in the covering materials by saturation of the sorption sites or decrease in the precipitation capacity of the metals should be minimized with successive intermediate covering, common practice in landfills operation.

The replace of soil by kraft pulp mills dregs and grits or lime mud represent in a significative costs decrease for the industry and for the municipalities and environmental advances for both.

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Capítulo 2

Aerobic biological treatment of municipal solid waste landfill leachates using kraft pulp mill *dregs and grits* as intermediate cover material

Abstract

The leachate is an important environmental aspect in landfills, containing many contaminants, among there high organic and inorganic compost, as metals, and it should be treated prior to being released into water bodies to avoid environmental damages and to health public. Heavy metals can be yet inhibit the microrganisms activity in the leachate biologic treatment. Therefore, the use of covering material for sanitary landfills with heavy metals removal potential is interesting. The soil, traditionally used as a covering material in landfills, presents a good metals retention, but it extraction in differents sites generate degradation problems, involving high repair costs. *Dregs and grits*, alkaline residues from the kraft pulp industry, were tested as intermediate cover material in MSW landfill experimental units. Two experimental units with 3 m high per 1 m diameter were built, being the unit 1 (U1) composed by interspersed MSW layers and a mixture of dregs+grits, 70% and 30%, respectively, and Unit 2 (U2) only contained MSW (control unit). The biologic treatment efficiency was evaluated through 2 aerobic reactors, with operation cycle of 24h, and the evaluated parameters were COD, pH, EC (Electric Conductivity) and SOUR (Specific Oxygen Uptake Rate). The average COD removals of 75% and 79% for the U1 and U2 leachates, respectively, were obtained. The SOUR was 0.33mg DO/g VSS.min for both leachates. This results suggesting that dregs+grits used as intermediate covering material do not affect the leachate biological treatment.

Keywords: landfill, leachate, solid waste, biological treatment, kraft pulp, dregs and grits

1. INTRODUCTION

Approximately 60% of municipal solid waste (MSW) generated in Brazil is disposed in sanitary landfills (ABRELPE, 2017). Sanitary landfill are engineered projects that ensure correct waste disposal, with low maintenance costs and environmental control (Yao, 2017). Leachate generation is the main environmental problem in landfills, with potential negative impacts on surface and groundwater sources (Kjeldsen et al., 2002).

Leachate is a dark liquid, generated from MSW organic matter decomposition, solid contaminants and rainwater that enters landfill (Yao, 2017; Moravia et al., 2013, Kurniawan, 2006; Blasco et al. 2017). Leachates have high organic and inorganic content, macro and micronutrients, mainly sodium and nitrogen, metals, phenols, organic xenobiotic compounds and microorganisms, such as total coliforms (Kjeldsen et al., 2002). The type, moisture and age of residues, landfill operation, climate, season, rainfall and groundwater intrusion may affect the characteristics and volume of the leachate (Im et al., 2001; El-Fadel et al. 2002). Volumes of 150 L of leachate per ton of MSW and 26,000 m^3/year were reported for landfills in Beirut, Lebanon (El-Fadel et al., 2002) and Jebel Chekir, Tunisia (Yahmed et al. 2009), respectively. In Brazil, the Seropedica landfill sanitary receive 9,000 t/day of MSW, generating a leachate volume of 1,000 m^3/day. (Pereira et al., 2018).

Landfill leachate requires treatment prior to being released into water bodies, being pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), electric conductivity (EC), ammonia nitrogen, solids and metals the main monitored parameters (El-Fadel et al. 2002). Biological processes (aerobic and anaerobic) are used for new leachates with high to medium BOD:COD ratio (Neczaj et al., 2005; Moravia et al., 2013), such as 39,500 mg/L BOD and 57,300 mg/L COD (0.7: 1) in Kerala, India (Arbabu et al., 2017). The recalcitrant biological fraction, found in more stable leachates and characterized by a low BOD:COD ratio is subjected to complementary physical-chemical treatment, such as advanced oxidative processes (AOP), reverse osmosis membrane filtration, precipitation, sorption and electrocoagulation, prior to being released into water bodies (Kurniawan et al., 2006; Li et al., 2011; Sanguanpak et al., 2006). The BOD:COD ratio is an important parameter regarding the leachate age, with variations from 0.05 to 0.8 guiding the appropriate mechanism for its treatment (Vazquez et al., 2004; Kjeldsen et al., 2002).

Soil is often used as intermediate and final covering material and is applied periodically over the waste mass in sanitary landfills, minimizing its scattering, odor and the presence of pathogen transmitting vectors. However, negative impacts are created in the areas from which it is removed (He et al., 2015).

Dregs and grits are alkaline residues generated in large volumes from pulp mills and have high management and final disposal costs. A total of 10 to 20 kg of *dregs* and *grits* are generated per dry ton of pulp (IPPC, 2013), most of which is disposed of in industrial landfills, increasing costs (Makitalo et al., 2014). *Dregs* and *grits* are rich in calcium carbonate (Cabral et al., 2008; Qin et al., 2015). *Dregs* have high concentrations of sodium and metals such as copper, chromium and nickel (Cabral, et al., 2008) and calcium carbonate (Martins et al., 2007). The use of alkaline residues, suck as dregs and grits, as intermediate covering of urban MSW landfills can be advantageous in the control of vectors, in the increase of metals retention capacity by chemical precipitation and in the preservation of areas by soil extraction reduction. Furthermore, the use of dregs and grits reduce the cost of the current industrial landfills.

The objective of this study was to evaluate COD removal efficiency of the leachates generated in two MSW final disposal experimental unit, with and without intermediate covering of dregs+grits in aerobic sequencing batch bioreactor.

2. MATERIAL AND METHODS

2.1. Leachate preparation

The leachates were generated in two MSW (municipal solid waste) disposal experimental units with three meters high and one-meter internal diameter, at the Universidade Federal de Vicosa. The leachates were collected in a drain installed in the lower base of the two units (Fig. 1). The U1 unit was filled with two 100 cm-layers of MSW, interspersed with two 20 cm-layers of a composed of 70% *dregs* and *30% grits* and the U3 (control) only contained MSW. The lower base of the two experimental units had 20 cm of gravel and the upper layer contained 40 cm of soil. The MSW was collected from the Vicosa municipality sanitary landfill, and its gravimetric composition determined and homogenized to fill the two units.

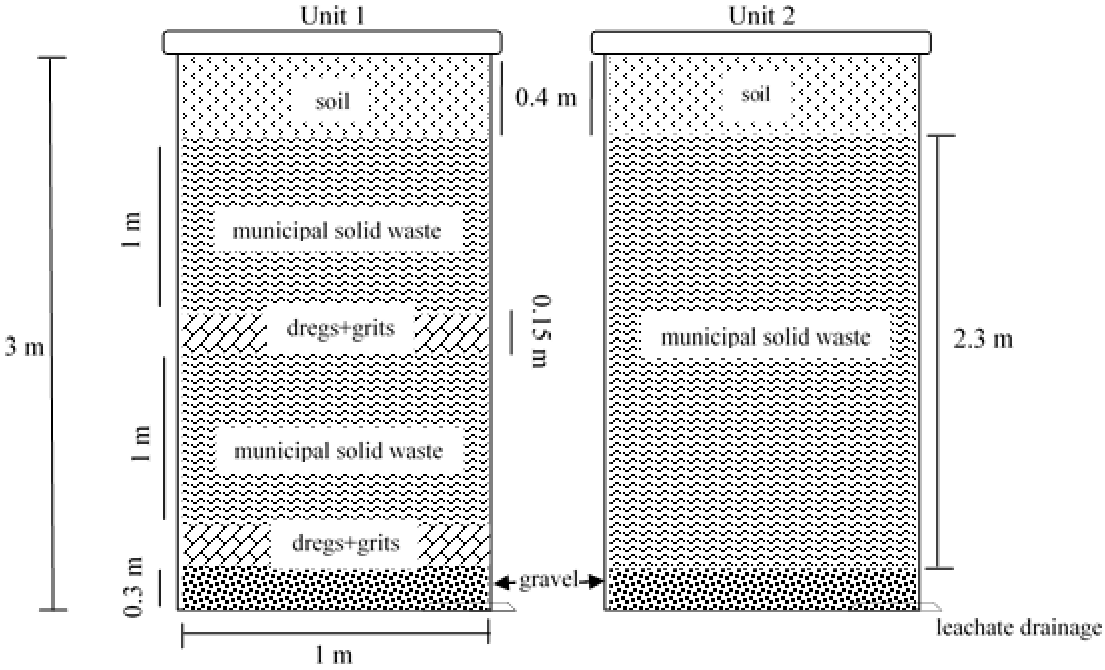

Fig. 1. Experimental units to generate the leachates treated in the biological reactors.

The elemental chemical composition of the residues (dregs and grits) was determined by Energy-dispersive X-ray spectroscopy (EDX) on SHIMAZU's EDX 1300 micro model spectrometer.

2.2. Biological treatment

The treatment of the leachates from the two experimental units was carried out in two aerobic sequencing batch bioreactors (Fig. 2), made of polypropylene, with a 2 L volume. Bioreactor R1 treated leachate from experimental Unit U1, and Bioreactor R2 leachate from Unit U2. An airflow aeration system was installed at the base of the reactors, overlaid with a perforated rigid plastic disk. A solenoid valve dispensed the supernatant (treated effluent) and the temperature in the reactors controlled using a thermostat and a submersible heater.

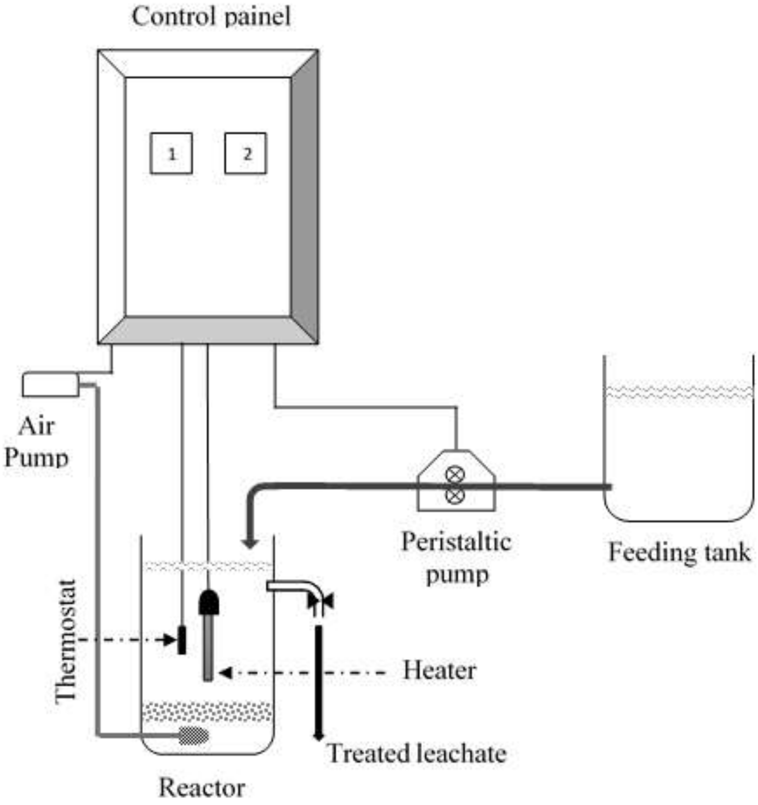

Fig. 2. Scheme of the aerobic sequencing batch biological reactors for leachate treatment

The bioreactors operated in a batch mode, with 23 h of aeration, 55 min of sedimentation and 5 min to discard the supernatant (treated leachate) making up a 24 h cycle. The reactors were started with 800 mL of sludge, generated in the control experimental unit (U3) and 600 mL of leachate, discarding 600 mL per cycle (supernatant). A peristaltic pump, driven by a control panel responsible for all operations in the treatment cycle (air pumps, heaters, thermostats and peristaltic pump) was used to fill up the reactors. Sulfuric acid was used to neutralize the leachate pH on reactors, keeping pH in the range of 6 to 8 during the 24 h cycle, until the eleventh monitoring interval. The operating temperature of the two reactors was kept at 30°C by a thermostat installed inside each reactor and connected to the control panel with 50 W power submersible heaters. Dissolved oxygen (DO) was kept above 4 mg L^{-1} in both bioreactors. Nutrients (N and P) were applied dosing a solution of urea and monoammonium phosphate in the leachate feeding tanks, using a (COD:N:P) ratio of 250:5:1.

The bio-sludge used on Reactors R1 and R2 was collected from a bioreactor of an activated sludge process of an eucalyptus bleached kraft pulp mill and a period of acclimatization of 7 days for each leachate at 30 °C was necessary.

The food: microorganism ratio (F/M) (kg COD/kg VSS) was 0.7 for the Reactor R1 and 0.4 for R2.

The bioreactor efficiency was measured by soluble COD removal. COD, pH, alkalinity and sodium content were determined according to Standard Methods for the Examination of Water and Wastewater (APHA, 2012).

In order to verify the biomass activity, respirometric tests of Oxygen Uptake Rate (OUR) were carried out in triplicate assays for the leachates from Reactor R1, according to the Standard Methods for Water and Wastewater Examination (APHA, 2012).

A separate assay was carried out with an extension of the cycle of typical 24h to 48h and 72h period in order to verify the bio-treatability capacity of the leachate. This assay was carried out in Reactor R1 in triplicate, operating during the period of the maximum efficiency, after the biological acclimation interval. Assays were carried out with different F/M ratios in order to establish the maximum F/M ratio without jeopardizing the biological system.

2.3. Specific Oxygen Uptake Rate (SOUR) assays

The microbiological kinetics of the organic matter consumption from effluents, the activity metabolic and the microorganism’s growth can be determined indirectly by the rate of oxygen use, allowing the evaluation of potential inhibitors, such as toxic elements. This method is used to guide the design of biological treatment systems for effluents, such as activated sludge (Garcia-Ochoa et al. 2010). The SOUR was calculated from Oxygen Uptake Rate (OUR), by respirometric test, over volatile suspended solids (APHA, 2012).

The SOUR was made comparing leachates of the Reactores R1 and R2 with F/M ratio of 0.1. On sequency, it was made only for R1, with F/M ratio varying from 0.3 to 2.3 (kg COD/kg VSS).

3. RESULTS AND DISCUSSION

3.1. Composition of dregs and grits

Carbonate and calcium oxide predominated in the *dregs and grits* (Table 1), characteristic of the chemical recovery process of converting the black liquor into white liquor, which returns to the digester (Cardoso et al., 2009; Kinnarinen et al. 2016), as reported for two kraft pulp mills in Finland (Golmaei et al., 2017). Dregs presented 30% - 40% of CaO in pulp mill in Sweden (Makitalo et al. 2014). The pH neutralization capacity in acid soils using dregs and grits, due predominance of calcium oxide and carbonate in this materials (Zhu et al., 2016), can be used with the same purpose in landfills, with metals retention potencial by chemical precipitation mechanism. This used can improve the leachate biological treatment conditions. The alkaline materials such as dregs has been used in permeable reactive barrier for metals removal, notably for acid mine drainage remediation. (Wang et al., 2016).

Table 1: Elemental chemical composition of dregs and grits used as intermediate covering in the MSW experimental units

	Compound/Element (%)										
	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SiO_2	P_2O_5	CO_3	Cl^-	SO_3
Dregs	0.46	33.17	1.24	0.49	1.99	2.36	4.09	0.02	49.38	0.22	3.72
Grits	0.22	53.65	0.64	0.35	0.50	2.13	3.93	0.03	34.28	0.19	0.71

3.2. Characterization of the leachate

The leachate COD from U1 was higher than from U2 (Table 2). The leachates had the same age, but the organic matter degradation process on Unit U1 was slower than U2, probably due the high sodium content, eleven times higher than U2. It resulted in different rates of food and microorganisms, since the reactors worked with the same volume of sludge and leachate. The presence of sodium is associated with the applied sodium sulphide and sodium hydroxide during the kraft pulping process for wood delignification. The alkalinity of the leachate U1 was five times greater than U2 (Table 2), suggesting potential metals removal by precipitation mechanism, improving the conditions for the biological treatment of leachate. The pH was similar for both leachates, between 7.0 and 8.0, typical of methanogenic stage stabilization in MSW landfills (Cuevas et al., 2009; Lindmark et al. 2014). Stabilization of leachate organic fractions in landfills is characterized by a pH of 4.7 to 8.8, representing acetogenic and methanogenic stages, respectively (Alver and Altas, 2017). The electric conductivity (EC) of the Unit U1 was 4 times higher than U2, suggesting the sodium presence in high concentrations, interfering on the biological treatment efficiency (Quartaroli et al., 2016).

Table 2. Characterization of the leachates used on biologic treatment assay.

	COD (mg/L)	pH	EC (mS/cm)	ST (mg/L)	Na (mg/L)	Alkalinity (mg/L $CaCO_3$)
U1	18,000	8.0	3.4	4,400	12,480	25,400
U2	10,000	7.6	0.8	1,350	870	5,000

3.3. pH and COD

The pH in Reactor R2 was kept neutral (6 to 7) at the beginning until the end of each treatment cycle, differing from Reactor R1, that end up with values of approximately 9 (Fig. 3). The buffer effect of the *dregs* (Zambrano et al. 2010; Cabral et al., 2008; Zambrano et al., 2007) in the leachate used in Reactor R1 has influenced this comportment. Optimum pH range for aerobic biological treatments is 6 to 8 (Metcalf and Eddy, 2003; Von Sperling, 2016), and high pH can inhibit the development of microorganisms in bioreactors, requiring neutralization with acid. It was required a dosage of 0.02 L of H_2SO_4 per liter of leachate to keep the Reactor R1 pH under 8.

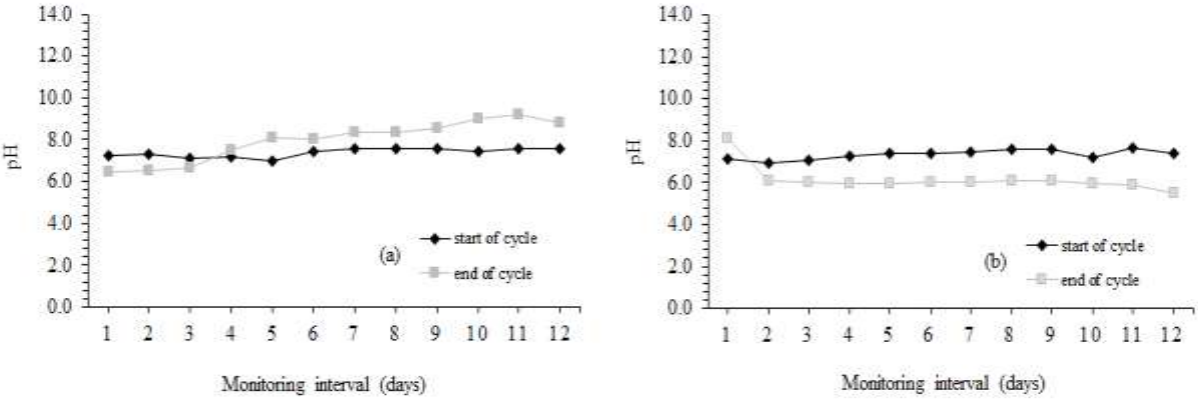

Fig. 3. pH variations measured at the beginning and end of the cycles in Reactors R1 (a) and R2 (b).

The COD removal efficiency on Reactors R1 and R2 started with 60% and 56% and increased on the 6th day to 93% and 87%, respectively. An average efficiency of 80% for both reactors were observed until 13th day (Fig. 4). The COD removal efficiency reduction of the reactors, notably in Reactor R1, may be attributed to the pH variation from the 11th day of monitoring, passing from the range of 6-8 to 6-9 (Fig. 3).

The average concentration of the feeding leachate COD of Reactor R1 was 18,400 mg/L and the treated leachate was 4,400 mg/L, while in Reactor R2, the feeding leachate COD was 11,400 mg/L and the treated leachate was 2,200 mg/L. The different food: microorganisms (F:M) ratio on Reactors R1 and R2 (0.7 and 0.4 kg COD/kg VSS) did not interfere on the treatment efficiency. Complementary systems are commonly applied to remove the recalcitrant and inorganic fraction, such as reverse osmosis, with efficiency above 95% (Dong et al. 2014).

A COD removal efficiency of 83% to 88% was found in aerobic biological reactors, with COD of 8,500 mg/L and F:M ratio of 0.43-0.62, treating landfill leachate from Liulitun Landfill, China (Zhu et al., 2013). Average removal of 50% was achieved for intermediate-age leachate with COD of 3,500-6,400 mg/L at the Papan Landfill in Malaysia (Yong et al., 2018), showing consistency between age of the leachate and the efficiency of COD removal.

The results of the present research suggests that dregs+grits used in intermediate covering of MSW did not cause negative interference on the traditional leachate biological treatment (Vasquez et al. 2014).

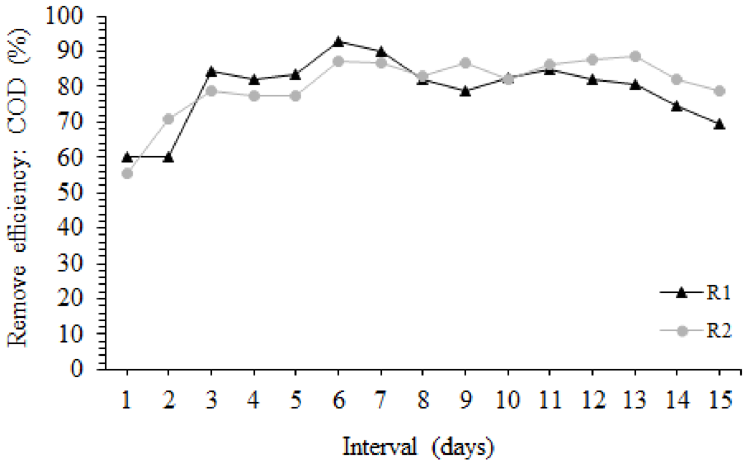

Fig. 4. COD removal efficiency of the leachate in biological reactors 1 and 2

The extended batch cycle period (48 h and 72 h) assay did not cause any further increase on the COD removal efficiency in Reactor R1 (Fig. 5), suggesting that 24 h is sufficient to remove completely the biodegradable fraction of the leachate (Fig. 4). COD removal of 67% to 87% was found for synthetic leachate treated in sequential batch bio-reactors, with aerobic granular sludge and activated sludge, respectively, with an operation cycle of 5.5 h (Ren et al. 2017).

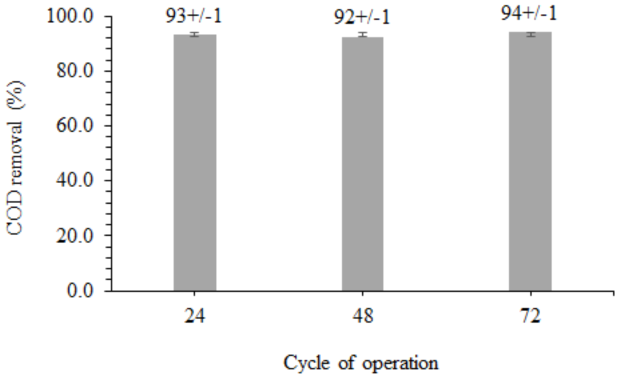

Fig. 5. COD removal efficiency in Reactor R1 with 24h, 48h and 72h cycle period

3.4. *Specific Oxygen uptake rate (SOUR)*

The Specific Oxygen Uptake Rate (SOUR) of the sludge samples collected in Reactors R1 and R2 had the same value of 0.33 mg DO/g VSS.min based in Oxygen Uptake Rate (Fig. 6). The volatile suspended solids (VSS) was 1,700 mg/L and 1,460 mg/L on Reactors R1 and R2, respectively. The SOUR can be used as a tool to indicate the biomass activity and growth (Gikas and Livingston, 1998), determining any inhibition caused by toxic element present in the leachate. No inhibition was observed in Reactor R1 compared to Reactor R2 (Fig. 6).

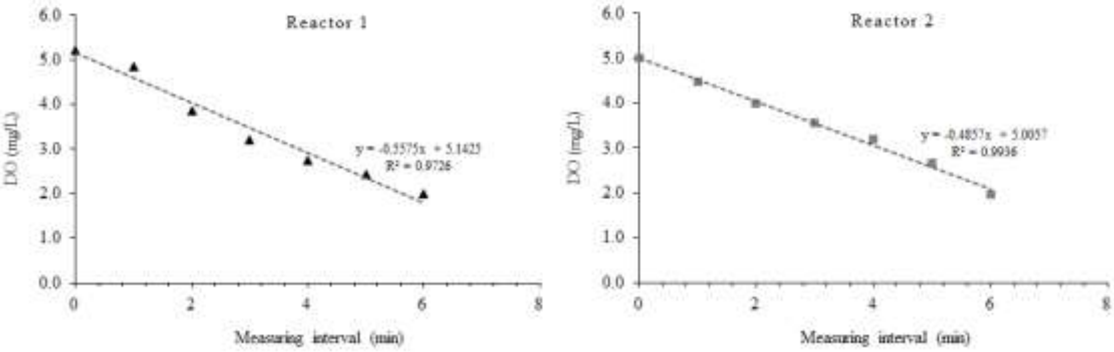

Fig. 6. Specific Oxygen uptake rate (SOUR) in the Reactors R1 and R2

SOUR assays carried out with different F/M ratios (Fig. 7) showed that up to a F/M ratio of 2.3 kg COD/kg VSS did not present any decrease in the biological activity, showing that the microorganisms were not inhibited by the leachate.

The Specific Oxygen Uptake Rate (SOUR) for the leachate from Unit U1 presented similar results for all different F/M ratios, from 0.3 to 2.3 kg COD/kg VSS (Fig. 7) suggesting that *dregs+grits* did not cause negative effect on the biological treatment.

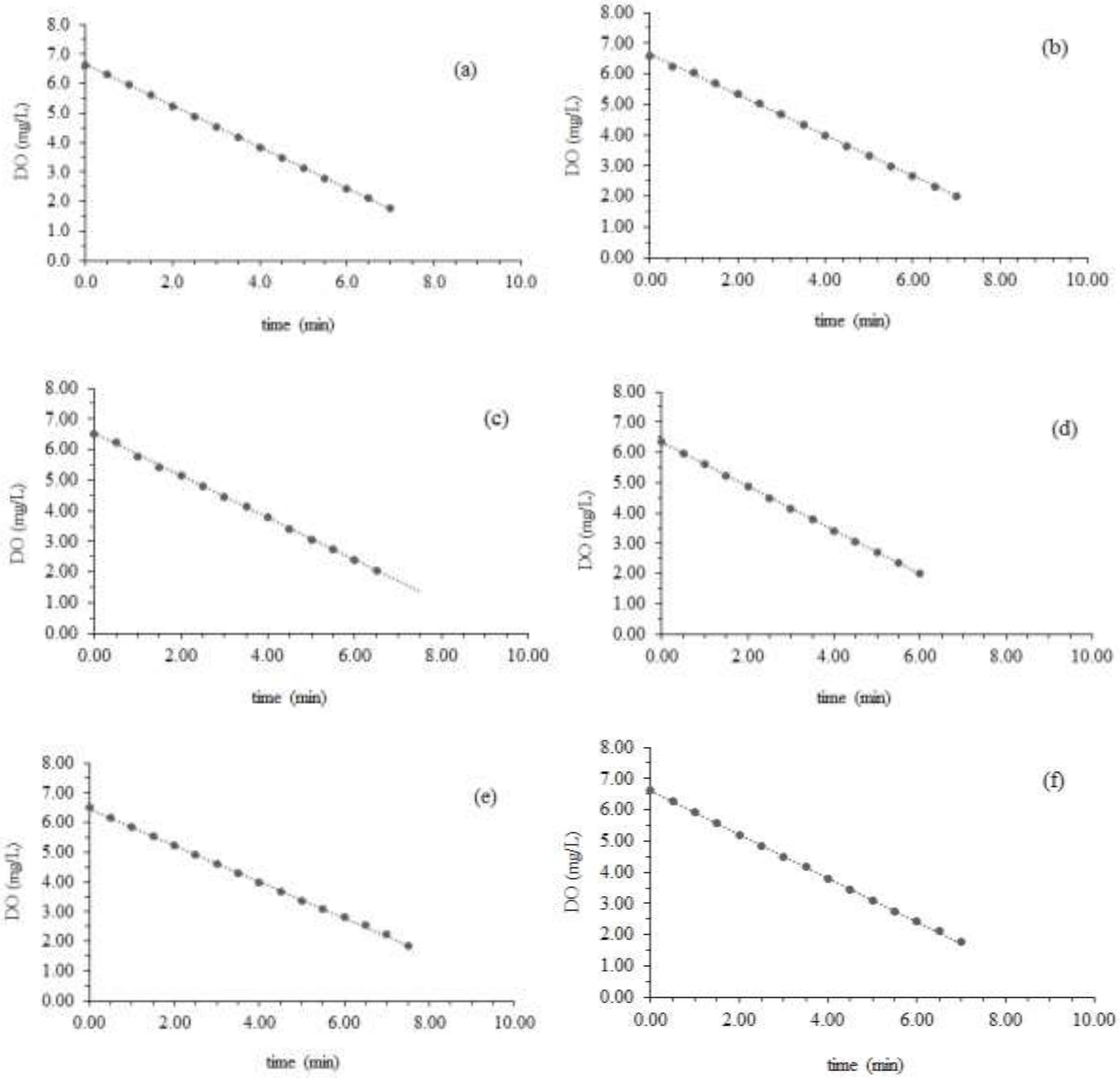

Fig. 7. Rate of oxygen consumption in Reactor R1 for different F/M (kg COD/kg VSS) ratios (a): 0.3; (b): 0.6; (c): 0.9; (d): 1.1; (e): 1.7 and (f): 2.3.

4. CONCLUSIONS

A mixture of *dregs+grits* can be used as intermediate covering in landfills, without jeopardizing the biological activity in the leachate treatment reactors.

A dosage of 0.02 liter of sulfuric acid per liter of leachate was necessary for pH neutralization in Reactor R1, treating the leachate generated on Unit U1 with intermediate cover of dregs+grits.

The increase of F/M ratio up to 2.3 (kg COD/kg VSS) did not reduce the biological activity on Reactor R1.

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Capítulo 3

Dregs, grits and lime mud use to heavy metals removal in landfills leachate

ABSTRACT

The surface and groundwater contamination by sanitary landfills leachate present negative impacts, due environmental damage and public heath risks, notably by heavy metals, such as Cd, Cr and Pb. Therefore, the metals removal of the leachates is necessary, including the improvement of the leachet quality for its biologic treatment, technology commonly used. Dregs, grits and lime mud, wastes generated in the kraft pulp mill, presents metals removal potential by chemical precipitation mechanism due to the alkaline characteristic. The aim of this study was evaluated the metals removal capacity in sanitary landfill leachates using a mix of dregs+grits, 70% and 30%, respectively, and lime mud, as intermediate cover material. Batch and column tests were carried out. A solution with leachate generated in an experimental sanitary landfill and metals (Cd, Cr, Cu, Ni and Pb) was prepared The batch test was carried out with solid: liquid ratio of 1:10 (4g: 40mL). The column tests were carried out, using 3 columns for each material (dregs+grits, lime mud and soil), with 18 applications of 80 mL per column. Metals retention on columns assays was above 80% for lime mud and soil, except for Cu in the lime mud columns until 12th application. The dregs+grits columns presented Cu desorption and low retention for Cd and Cr for 70% initial percolated volumes. However, all parameters evaluated presented values bellow of the limits to release in water bodies, according the brasilian legislation, suggesting a potential of dregs+ grits and lime mud for metals removal in sanitary landfill leachates.

Keywords: landfill, leachate, metals, waste solid, biologic treatment

INTRODUCTION

The kraft pulp production in Brazil was 18.8 million tons in 2016, the second world's largest producer (IBA, 2017). The kraft process is the most widely used in the world, with extraction of the cellulose in alkaline medium, by the application of sodium hydroxide and sodium sulfide at high temperatures (Lopes et al., 2017; Larsson et al., 2015; Castro et al., 2009). In the process of chemical recovery of these compounds, three alkaline wastes are generated: dregs, grits and lime mud (Martins et al., 2007; Poykio et al., 2006), presenting high treatment and final disposal costs for the factories.

Incineration processes take advantage of the energy potential of the wastes (Singh et al., 2011) and reduce their volumes by more than 90%. However, the incineration can generate air emissions and concentrate the toxic elements in the ashes, such as metals, with risks for the human health and the environment (Yang et al., 2009; Okada et al., 2007), demanding significant costs for implantation and operation of air emissions control systems (Li et al., 2015). On the other hand, the recycling or reuse of dregs, grits and lime mud can present an attractive option to reduce this environmental liability of pulp mills.

The use of these wastes as intermediate covering material in sanitary landfills of municipal solid waste (MSW) was proposed, replacing soil, commonly used material (He et al., 2015). The intermediate covering of the MSW is a standard practice in landfills operation, avoiding the dispersion of contaminants by wind action, contamination of adjacent areas, presence of disease vectors and bad odors (He et al., 2015).

The leachate is a dark liquid, generated by rainwater percolation into sanitary landfill cells, by the organic matter biostabilization and leaching of the MSW constituents (Yao, 2017). It has a complex composition, such as different organic compounds, macro and micronutrients, phenols, aromatic hydrocarbons and metals (Christensen et al., 2001; Dan et al., 2017).

Metals, such as Cu and Zn, are essential to the development of plants, occurring naturally in rocks, soils, surface water and groundwater (Kintlová et al., 2017), but in high concentrations can cause toxicity to humans and to the environment. Chromium is a potentially carcinogenic element and has a relation with damage to genetic material, hypertension and deleterious effects on hemoglobin (Fedan e Cutler, 2001; Wang, 2008). Lead boosts cancer risk (Silbergeld, 2000) and is associated with damage to the nervous system (Hanninen et al., 1998) and may cause cognitive impairment (Lanphear et al., 2000). Cadmium, and nickel have mutagenic effects in humans and in other species (Beyersmann, 2008). Metal ions have potential to act as enzyme inhibitors (Prakash et al., 2008), and may interfere on cellular metabolism of microorganisms responsible for biological treatment of the leachate. Metals accumulate in human cells, causing different damage to health (Da’na, 2017; Uçer et al., 2006). Physical, chemical and biological technologies, such as chemical precipitation, coagulation, ion exchange, membrane technology, complexation and adsorption, for removal these elements, notably for low cost materials, have been used (Uçer et al., 2006; Peng et al., 2017; Mustafa et al., 2010).

The adsorption mechanism consists in the separation of an undesired element or substance, especially metals, occurring on interface between the solid and aqueous media, involving two main mechanisms: specific adsorption, by complexation, and non-specific, by means of electrostatic force, based on external sphere mechanism, less stable than specific adsorption (Bradl, 2004; Echeverría et al., 1998). Adsorption mechanisms presents low operation cost and high efficiency on metals removal from aqueous medium (Carolin et al., 2017).

Activated charcoal and biochar have been used as adsorbents for different elements, such as chlorine and metals (Amerkhanova et al., 2017; Kolodynska et al., 2017). Sugarcane bagasse, coconut, sawdust and aquatic algae have been studied and applied as adsorbent materials for toxic materials (Uçer et al., 2006; Axtell et al., 2003), and inorganic adsorbents like zeolites, have been successfully applied in the removal of metals in aqueous media (Nakamoto et al., 2017).

The objective of this study was to evaluate the potential of the dregs+grits mixture and lime mud in the retention of metals on leachate generated in an experimental MSW landfill, built on Universidade Federal de Viçosa, Brazil.

METHODOLOGY

Preliminary assays: physical and chemical characterization of the leachate

The leachate used in the batch adsorption tests and columns tests was sampled on a experimental landfill cell, three months after its filling with MSW.

Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), alkalinity, pH, total solids (TS), total fixed solids (TFS), total volatile solids (TVS), fixed suspended solids (FSS), volatile suspended solids (VSS) and ammoniacal nitrogen were analyzed (APHA, 2012). The concentrations of Cd, Cr, Pb, Zn, Ni, Cu e Na of the mixture of dregs+grits and from lime mud were determined, according to the Standard Methods 3111B e SM-3500-Na B (APHA, 2012).

Preparation of the adsorbents

The adsorbent materials were dried at 60°C and then crushed at 150-425 µm for dregs+grits, 53 - 153 µm for lime mud and 1,000 µm - 2,000 µm for soil. The chemical characterization of the alkaline by-products was done by X-ray dispersive energy spectrometry (EDX) in SHIMAZU's EDX 1300 micro model spectrometer.

Batch adsorption test

A ratio of 1:10 (4 g of adsorbent:40 mL of leachate) was used in the adsorption assays of As, Cd, Cr, Cu, Ni and Pb by dregs+grits, lime mud and soil (Dias *et al.* 2001 e Joris *et al.* 2012). The samples were shaking in horizontal table at 150 rpm for 24 h and centrifuged at 3,000 rpm for 10 minutes, followed by filtered in Whatman 40. The samples were digested with nitric (HNO_3) and perchloric ($HClO_4$) acid, in a plate heated to 250°C.

The metals solution was prepared with leachate and metals: Cd (1.0 mg/L); Cr (3.0 mg/L); Cu (0.1 mg/L); Ni (3.0 mg/L) and Pb (0.5 mg/L). This metal concentrations were previously inserted into the software Visual MINTEQ2® for simulate possible precipitation of oxides or hydroxides. The concentrations of the metal ions of the samples were determined in optical emission spectrophotometer with coupled induced plasma, Perkin Elmer model Optima DV 7300.

Columns test

The solution of leachate and metals was prepared the same conditions of the batch assays, including 5.0 mg/L of Mn. The determination of metal concentrations followed the same method as the batch test.

Preparation of the columns

The adsorption columns were built in PVC pipes, with 7.5 cm of internal diameter by 40 cm of height. Each column was filled with 20 cm of adsorbent material (soil, lime mud or dregs+grits). On lower bases from columns were installed a plastic cap perforated to allow the drainage of the leachate. A glass wool disc was installed on the top and at the base of each column (Figure 1).

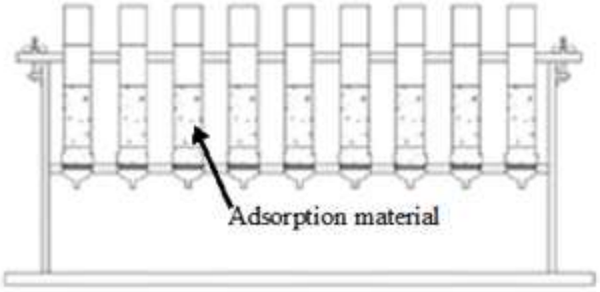

Figure 1. Adsorption columns test

Prior to the leachate solutions application, the columns were saturated by immersion in deionized water. Preliminary tests indicated saturation volumes of 492 mL, 450 mL and 460 mL for dregs + grits, lime mud and soil, respectively.

Solutions application and percolates sampling

For each column, 18 applications of 80 mL of leachate and metals solution were carried out. After each application, the percolate was collected. Percolates of three samplings were mixed and formed one composite sample. By the end, 6 composite samples were obtained.

The percolate volume and pH of each column were monitored and digested with nitric acid (HNO_3) and perchloric acid ($HClO_4$) at 250°C (APHA, 2012). The parameters Cd, Cr, Cu, Mn, Ni and Pb were determined in Agilent Technologies model 240 AA Atomic Absorption Spectrophotometer.

Desorption column tests

The desorption tests were carried out percolating 240 ml of deionized water with pH 5 in each column, and the percolated analyzed with the same conditions of the batch adsorption test. Then the metals concentration (Cd, Cr, Cu, Mn, Ni and Pb) were analyzed by Atomic Absorption Spectrophotometry, Agilent Technologies, model 240 AA.

RESULTS AND DISCUSSION

The leachate used in the adsorption tests presented a COD of 9,856 mg/L, pH 8.3 and COD/BOD ratio of 4.3 (Table 1), characteristics commonly find in intermediate stabilization phase of leachates in urban landfills (Kjeldsen et al., 2002; Vazquez et al., 2004; Yao, 2017).

The pH and COD of the leachate used in the experiment ranged from 5.8 - 8.5 and 43.000 - 3.270 mg/L, respectively, during the six months of monitoring of the experimental landfill.

Table 1. Characterization of the leachate (mg/L)

COD	BOD	N	alkalinity	TS	TFS	TVS	TSS	FSS	VSS	pH
9,856	2,333	594	5,750	10,020	5,500	4,520	815	113	703	8.3

Carbonate and calcium oxide were predominant in the alkaline dregs+grits and lime mud used as adsorbent media (Table 2). Carbonate, calcium oxide, iron oxide and magnesium oxide are important sources for pH neutralization in acidic soils, controlling the metals mobility by adsorption and precipitation mechanisms (Zhu et al., 2016; Thakur et al., 2006; Suzuki *et al.* 2008; Bradl, 2004). Calcium oxide and carbonate are present in high concentrantions on dregs and lime mud (Jia et al., 2013; Qin et al., 2015; Martínez-Lage et al., 2016).

Table 2. Chemical characterization of alkaline by-products (*dregs*, *grits* and lime mud – L.M.)

	Element (% mass)										
	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SiO_2	P_2O_5	$CaCO_3$	Cl	SO_3
Dregs	0.46	33.17	1.24	0.49	1.99	2.36	4.09	0.02	49.38	0.22	3.72
Grits	0.22	53.65	0.64	0.35	0.50	2.13	3.93	0.03	34.28	0.19	0.71
L.M.	0.07	57.12	0.20	0.26	0.91	2.32	3.58	0.03	31.36	0.14	0.40

The sodium concentration in the dregs+grits mixture was 7.5 higher than in lime mud, and showed a higher concentration of Cr, Cu and Ni (Table 3). Metals such as Cd, Cr, Cu, Ni, Mn, Pb and Zn are present in dregs (Kasassi *et al*. 2008; Kinnarinen et al., 2016; Golmaei et al., 2018), usually with insoluble characteristics (Golmaei et al., 2017). The sodium in dregs and lime mud originates from the use of sodium hydroxide and sodium sulfide in the woodchips cooking stage for delignification and fiber separation in the kraft process (Golmaei et al., 2017).

Table 3. Metal concentrations in dregs+grits and lime mud used in the experiment (mg/kg)

MATERIAL	Cd	Cr	Cu	Ni	Na	Pb
Dregs+grits	<10	46.0	245.0	47.7	96,250	<10
Lime mud	<10	<10	<10	3.3	12,275	<10

Batch adsorption test

Dregs and soil presented retention higher than 83% for all metals, except for Ni, being 73% and 72%, respectively. The lowest retention was verified for Ni (35%) in lime mud, and the higher for Cr (96%) in soil. (Figure 2). The application of dregs as permeable reactive barrier in plumes of underground contamination was proposed, mainly by the buffer effect, suggesting the metals removal by precipitation mechanism. The buffer capacity is due main to the calcium and calcium carbonate presents in dregs and grits (Golmaei et al., 2017). The metals precipitation in this study can be occour with free hydroxyls (OH^-) in hydroxides form and sulfide precipitation, using the sulphur present in dregs and grits, such as lead sulfide. However, to the sulfide precipiatiation mechanism is necessary to sulphur reduction by acidophilic chemolithotrophic microorganisms (Ye et al., 2017), it condition not verified for the present experiment. The sulfide precipitation can be formed using sodium and ammonium too, compounds present in landfill leachates, it competing with metals on precipitation mechanism (Makitalo et al., 2014; Golmaei et al., 2017; Lewis, 2010). Lime mud presented high retention of Cr (94%), Cu (99.6%) and Pb (96.8%) in metal finishing wastewater with initial concentration os 39 mg/L, 67 mg/L and 1.3 mg/L, respectively, by sorption and chemical precipitation (Sthiannopkao e Sreesai, 2009). It results were similar to the present study, indicating potential for the proposed application. The chemical precipation is a fast and selective mechanism widely used by industries to metals removal from wastewater (Liu et al., 2018; Lewis, 2010). Impermeability effects can be caused by the small particle sizes and plastic structure of the dregs, demanding a mixture with other materials, such as grits (Modolo et al., 2010).

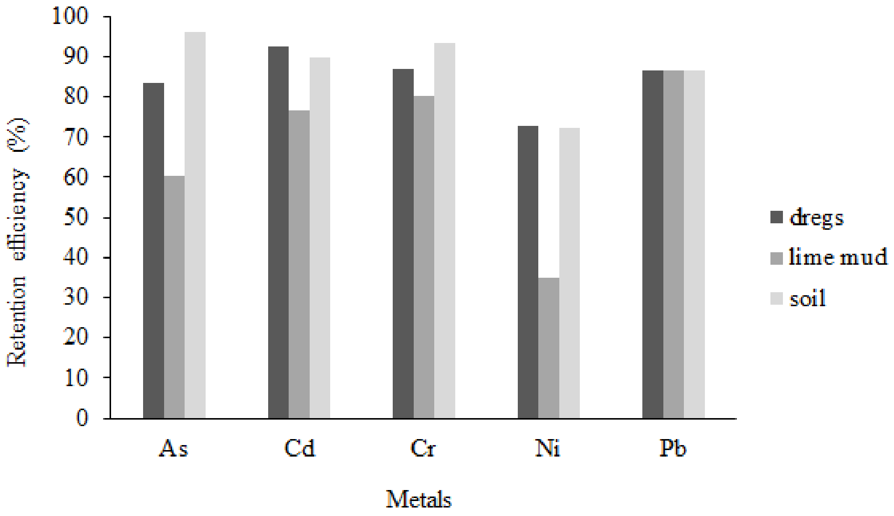

Figure 2. Efficiency of metals sorption by dregs + grits, lime mud and soil

Adsorption column test

For each two composite percolate samples was calculated an average, resulting in 3 average values of metals retention. The Cd, Cr and Mn retention were above 95% for soil and lime mud during all column tests. In the dregs column, the Cd retention ranged from 22% to 72%, from 10% to 97% for Cr and above 94% for Mn. The Ni and Pb presented a similar decrease behavior for the lime mud columns, suggesting the adsorption material saturation, differs from soil, with 100% of Ni retention during the test. There was a desorption of Cu during all dregs column tests. The same behavior occurred for Cr in the 2nd and 3rd applications on columns filled with dregs (Figure 3).

The difference verified for metals retention efficiency between dregs+grits and the others adsorption materials (lime mud and soil) can be justified by the high sodium concentration (96,250 mg / kg) in this material, eight times higher than lime mud, competing for sorption sites as well as hydroxides and sulfide precipation (Zhang et al., 2017; Lewis, 2010). Dregs+grits presented an average retention of 80% in the batch adsorption tests and 62% in the column adsorption tests. This difference can be explained by the contact time, higher in batch tests than in the column tests, resulting in sodium ion exchange, behavior commonly verified in the soil matrix (Kolodynska et al., 2017; Suzuki et al., 2008).

Industrial wastes have been studied as adsorbent materials due to their low cost and large quantities, such as lime mud, with high retention capacity of metals in wastewater (Carolin et al., 2017). Lime mud was applied in soil for pH neutralization, reducing the mobility of metals, such as cadmium, copper, nickel and lead, by precipitation mechanisms (Gray et al., 2006).

Soil is a good adsorbent of metals, especially by the structure consisting of organic and inorganic colloids, oxides and metal hydroxides, such as iron and manganese (Bradl, 2004; Uddin, 2017). The soil used as intermediate covering in landfills can retain metals present on leachate, with 99%, 94%, 55%, 53% and 49% removal for Cd, Pb, Mn, Ni and Cu, respectively. Experimental landfill cells using soil as intermediate covering presented lower metals concentration in the leachates than cells without soil (Suzuki et al., 2008). The heavy metals removal was higher in this study for soil and lime mud, reinforcing the potential of the alkaline wastes use, notably for lime mud. Factors such as soil type, type and concentration of metal ions and pH can be influence the adsorption capacity (Bradl, 2004). Cr, Pb and Cu are elements more strongly adsorbed by the soil matrix than Cd and Ni (Gomes et al., 2001), a condition different from that verified in this research, where Ni and Cd presented the highest retention for the three adsorbent materials studied. The maximum adsorption of Pb>Cd>Cu was observed for biochar adsorbent, with pH 5.0 (Kolodynska et al., 2017).

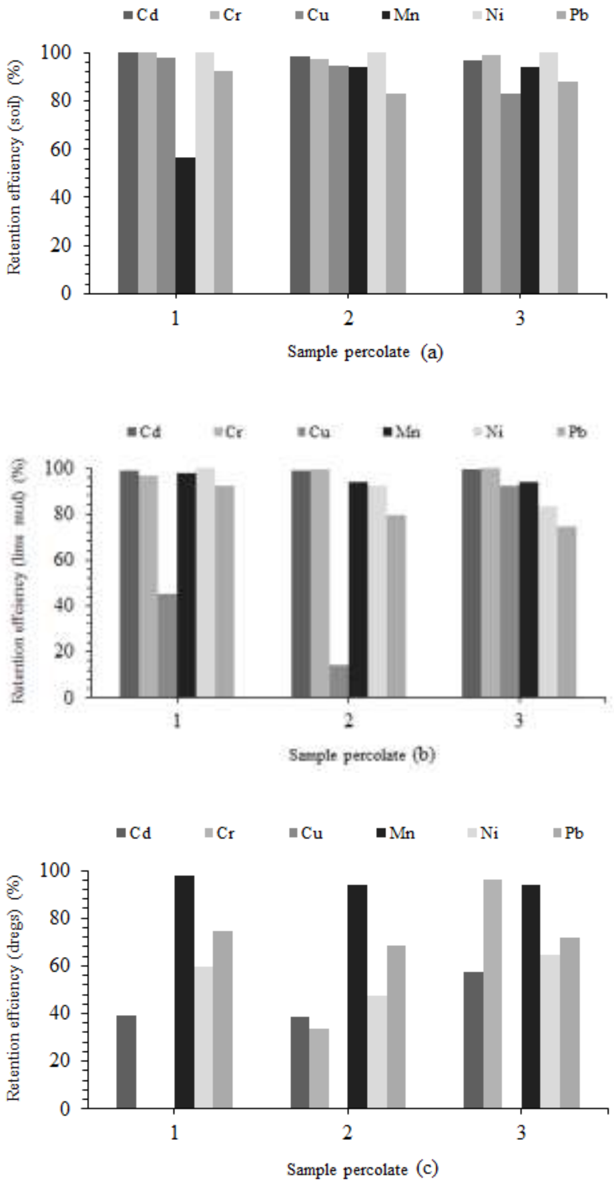

Figure 3. Metals retention on soil (a), lime mud (b) and dregs (c) columns

The pH of the percolated solution on the dregs+grits columns increased from 7.7 to 10.5 (36.5%), behavior maintained during the experiment (Figure 3a). The lime mud columns presented similar increase (36%), but reduced 18% at the end of the 18 applications (Figure 3b). The pH increased 1% on soil columns, remaining constant throughout the experiment (Figure 3c).

The buffer capacity of dregs+grits and lime mud is important for metals retention by precipitation mechanisms (Stigliani, 1996). An increased from 29% to 83% on Cu retention using wood sawdust in aqueous solution, with pH ranging from 2 to 4, was verified, increasing again up to 90% with pH above 7 (Rahman e Islam, 2009). Alkaline composts like carbonate and hydroxides, present in dregs and grits (Golmaei et al. 2018; Manskinen et al. 2011; Cabral et al. 2008; EPA, 2006), react with hydrogen ion, neutralizing or increasing the pH on solution and removing metals by precipitation mechanism (Torres et al. 2018; Gray et al. 2006).

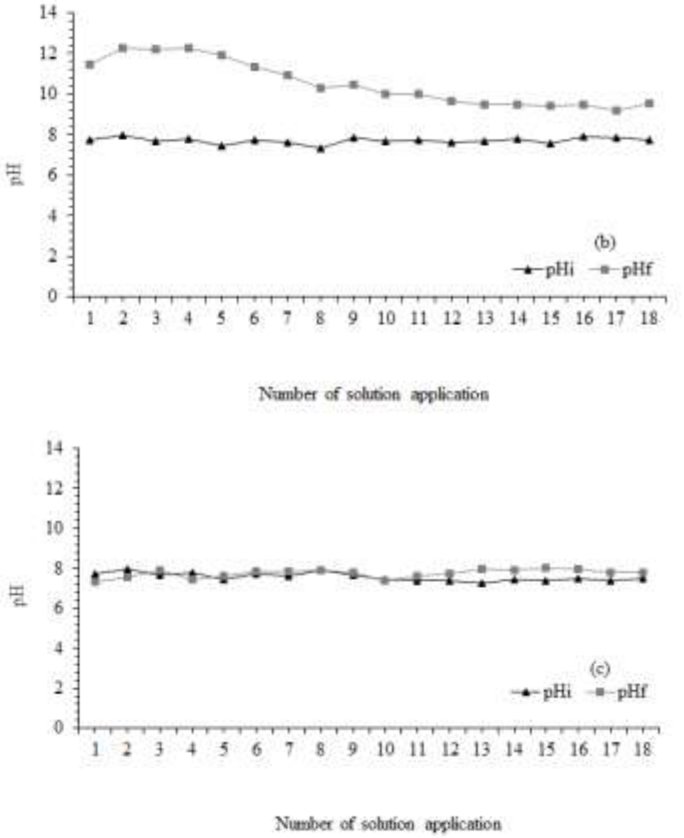

Figure 3. pH variation between the solutions applied and the leachate in the columns with dregs + grits (a), lime mud (b) and soil (c)

Metals desorption tests

The metals desorption for all columns were below 5%, except for Cu, that presented desorption in all dregs+grits columns (Table 5). The metal ions concentrations on percolates of the columns with dregs+grits, lime mud and soil, were below the limits recommended by the Brazilian legislation for the discharge of effluents in water bodies. The desorption study is important for evaluated the dissolution conditions, notably by natural causes, such as the rains. The sulphide precipitation presents low solubility in aqueous media, reducing the metals dissolution risks a long term. (Lewis, 2010), important condition to application proposed for dregs, grits and lime mud.

Table 5. Metallic ions desorption on columns with dregs + grits, lime mud and soil

		METALS					
MATERIAL		Cd	Cr (total)	Cu	Mn	Ni	Pb
	TAL (mg)	**1.44**	**4.32**	**0.144**	**7.2**	**4.32**	**0.72**
Dregs+grits	PL (mg)	0.019	0.043	0.147	0.205	0.076	0.005
	PL/AL (%)	*1.32*	*1.0*	*102.0*	*2.9*	*1.8*	*0.7*
Lime mud	PL (mg)	0.001	0.015	0.036	0.026	0.177	0.002
	PL/AL (%)	*0.1*	*0.4*	*25.0*	*0.4*	*4.1*	*0.2*
Soil	PL (mg)	0.003	0.006	0.008	0.089	0.013	0.004
	PL/AL (%)	*0.2*	*0.1*	*5.3*	*1.2*	*0.3*	*0.5*

Total Applied Load (TAL); Percolated Load (PL)

CONCLUSIONS

Dregs+grits and lime mud have a potential use as intermediate covering in landfills, reducing the metals load of the leachates. This implies on improve of the leachate biologic treatment and lesses costs with it treatment.

Lime mud showed the higher retention capacity and the lower desorption potential, compared to dregs+grits.

The concentrations for all metals on desorption test for dregs+grits, lime mud and soil were below the recommended limit for discharge of effluents in water bodies by the Brazilian legislation.

Dregs and grits has potential for metals removal in another industrial effluents, such as tubular furniture and tannery industry, being necessary complementary studies to evaluation specific concentration and multi-elmentars compositions.

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Capítulo 4

Use of kraft pulp mill dregs and grits as permeable reactive barrier for removal of and sulfate in acid mine drainage

ABSTRACT

Mining is an essential human activity but results in several environmental impacts, notably the contamination of ground and surface water by presence of substances such as metals and sulfates in acid drainage waters. Permeable reactive barriers (PRB) have been applied to remediate this environmental impact but the high costs associated to the maintenance of this system are still a challenge. The main objective of this study was to evaluate the use of kraft pulp mills alkaline residues named dregs and grits as material for PRB and determine the capacity to retain copper and sulfate. The work was carried out in laboratory adsorption kinetics essays, batch assays and column tests. The elemental characterization, point of zero charge, acid neutralization capacity, total porosity, bulk density and moisture of the dregs and grits were carried out. The results showed high retention of Cu due chemical precipitation mechanism, notably for dregs (99%) at 5 min in adsorption kinetics. The grits presented similar results after 180 min for the same assay. Sulfate retention was effective at pH bellow 5, with efficiency of 79% and 89% for dregs and grits, respectively. Dregs presented the best results to acid drainage remediation, notably for solid:liquid (S:L) ratio of 1:50.

1. INTRODUCTION

Acid mine drainage (AMD) is caused by oxidation of metal sulfides in the presence of oxygen and water, resulting in sulfate formation and metals solubilization, by acidification of the medium (Kaur *et al.* 2018; Mamelkina et al. 2017; Shabalala et al. 2017; Fungaro and Izidoro, 2006).

Active and inactive mining areas, such as copper, lead, zinc, gold, silver and uranium, with potential for degradation of the environment by the presence of different contaminants, particularly metals and sulfates presents in acid drainage (Antunes and Albuquerque, 2013).

The acid drainage formation is an important environmental aspect of mining practices, notably by the presence of metals and high concentrations of sulfates. The sulfates concentration range from 2,400 to 20,800 mg/L (Pino et al., 2018; Fernando et al., 2018), well above the limit of 250 mg/L established by the World Health Organization (US EPA, 2017). It might cause damage to public health and to the environment and depreciation of structures and equipment (Mamelkina et al. 2017; Silva et al. 2010; Wilkin and McNeil, 2003), resulting in high costs for control and management by the mining companies (Torres et al. 2018; Nordstrom, 2011; Silva et al. 2010). The Cu concentration range from 77 to 615 mg/L, with major values on the cooper mines (Kaur et al., 2018; Vital et al., 2018). Other metals such as Al, Mn, Fe, Mg and Zn are commonly found on the acid drainage in these mines (Crane e Sapsfordb, 2018; Torres et al., 2018).

The AMD remediation can be actively accomplished out site with the pumping of the contamination plume to a treatment plant, or passively, on site with the use of permeable reactive barriers (PRB), with lower installation and maintenance costs. It can be carried out with the flow directed to the system, by the Funnel model, or the grid-type, by the installation of a perpendicular barrier to the contamination plume (Obiri-Nyarko et al. 2014; Thiruvenkatachari et al. 2008). The PRB was first proposed in Canada in the 1990s (Obiri-Nyarko et al. 2014; Vesela et al. 2006), with different materials used as adsorbent media, from single barrier material to composites of different materials, or multiple sequential barriers (Holmes et al. 2017; Han et al. 2016). Materials as activated carbon, zeolites, zero-valent iron, powder of cement furnace with quartz sand, have been studied for application in reactive permeable barriers (Karnib et al., 2014; Misaelides, 2011; Moraci and Calabrò, 2010; Sulaymon et al., 2015). The selection of adsorbent materials is determined primarily by the types of contaminants to be removed, the desired levels of removal, the costs, the shelf life of the materials and their regeneration potential (Vignola et al. 2011). The use of industrial wastes or by-products has been studied due to the low cost and the opportunity to increase the lifespan of these materials (Erdem et al. 2004), reducing the environmental pressure on final disposal methodos and natural resources exploitation. Those measures are in accordance to the principles of the Circular Economy, a policy with increasing application in the countries of the European Union.

PRB can be applied for the neutralization of pH and remediation of organic and inorganic contaminants, especially by mechanisms of adsorption, precipitation and biological degradation. They have as a main advantage the on-site treatment, and as a disadvantage, the lifespan of the adsorbent materials and the maintenance costs (Obiri-Nyarko et al. 2014; Thiruvenkatachari et al. 2008). High efficiency methods for sulfates and metals removal in acid mine drainage (AMD) have been proposed using individual or sequential PRB filled with limestone and $BaCO_3$, respectively, resulting in a complete removal of metals and more than 70% of the sulfate, by precipitation and adsorption mechanisms (Torres et al. 2018).

The dregs and grits, originated in the liquor chemical recovery of kraft pulp mills, have a high pH, from 10.5 to 13 (Cabral et al. 2008), and predominance of carbonate and calcium oxide (Martínez-Lage et al. 2016; Jia et al. 2013; Qin et al. 2015). Those characteristics potentiate the mechanisms of chemical precipitation and adsorption, suggesting an attractive application in the retention of metallic ions and sulfate (Zhu et al. 2016; Thakur et al. 2006; Suzuki et al. 2008; Bradl, 2004; Silva et al. 2010). Efficient metal removals such as Cd, Cr, Cu, Ni, Zn and Pb in solution, notably by precipitation mechanisms, are attributed to calcium carbonate (Aziz et al. 2008), with 93% average removal of Fe and Mn in aquifers contaminated by landfill leachate in the USA (Wang et al. 2016). Metals such as Cd, Cr, Cu, Ni and Pb were identified in samples of dregs and grits from a pulp mill in southern Portugal (Makela et al., 2016; Kinnarinen et al. 2016; Modolo et al., 2010). However their application in soil did not cause leachates with characteristics above the limits established by the European Council Directive 86/278 / EC, similar to the values found by the application of commercial limestone (Cabral et al. 2008).

This study proposes the use of kraft pulp mill dregs and grits as a reactive material in PRB. It is expected the simultaneous removal of Cu, Fe, Zn and SO_4 in acid mine drainage by precipitation mechanisms (alkalinity) and adsorption of sulfate by the positive charge of the adsorbent material surface, occurring when the adsorbate solution pH is lower than the zero charge point (PCZ) (Vieira et al. 2009; Cerovic et al. 2007).

2. MATERIAL AND METHODS

2.1. MATERIAL AND SAMPLE PREPARATION

Samples of dregs and grits (about 5 kg each) were collected in a pulp mill in the centre region of Portugal. Both samples were dried at 40°C until constant weight (NEN, 1995), milled and sieved to gather the fraction 0.5 to 1.0 mm (Torres et al. 2018; Ramos et al. 2017).

2.2. CHARACTERIZATION OF ADSORBENT MATERIALS

The adsorbent materials (dregs and grits) were characterized by energy dispersive X-ray fluorescent (EDXRF), using a NEX CG Rigaku Spectrometer, according to ASTM D4927.

Total Porosity

The total porosity of the adsorbent materials was determine by adapted method, weighting the columns filled only with materials and next saturated with kerosene (Torres et al. 2018). A graduated test tube was filled with 10 mL of adsorption material and weighted. Subsequently, it was added kerosene until the material saturation, and the tube was weighted again. The total porosity was determined by the Equation 1.

$$total\ porosity = \frac{\left(\frac{\mathrm{Pf-Pi}}{\mathrm{kerosene\ density\ (g/mL)}}\ x\ 100\right)}{volume\ material\ (mL)} \qquad \text{Equation 1}$$

were:
Pi: weight initial
Pf: weight final

Acid neutralization capacity

The buffering capacity of the adsorption materials was determined with the batch titration method, using 0.75 g of dregs and grits to 20 mL of deionized water, shaking for 24 h. The titrations were from 0 to 16 mL of HCl, 1 mol (Makitalo et al. 2014).

Following this procedure, the buffer capacity was measured across pH variation in different S:L (Solid:Liquid) ratios (1:10, 1:20, 1:50, 1:100 and 1:1000), stirring by 24 h at 100 rpm.

Point of zero charge (PZC)

The point of zero charge of dregs and grits was determined adding 0.1 g of each adsorbent material and 20 mL of KNO_3 solution (0.01 mol) in a plastic vial of 50 mL, and shaking for 24 h. Plastic vials were prepared, with initial pH ajusted from 2 to 12. The pH_{PCZ} was determined when pHΔ (pHf – pHi) was zero. If pH_{PCZ} is smaller than the solution pH, the adsorption materials presented negative charge, attracting cationic ions, and in opposite situation, the materials will have a positive charge, attracting anionic ions (Soares et al. 2016; Vieira et al. 2009; Cerovic et al. 2007).

2.3. EXPERIMENTAL STRUCTURE

The laboratory continuous upflow column test was used to simulate the reactive effect of the adsorbent materials used as permeable reactive barrier – PRB (Shabalala et al. 2017; Han et al. 2016; Sulaymon et al. 2015; Zhou et al. 2014; Cavaco et al. 2007). A column with 32 mm x 100 mm was assembled (Figure 2).

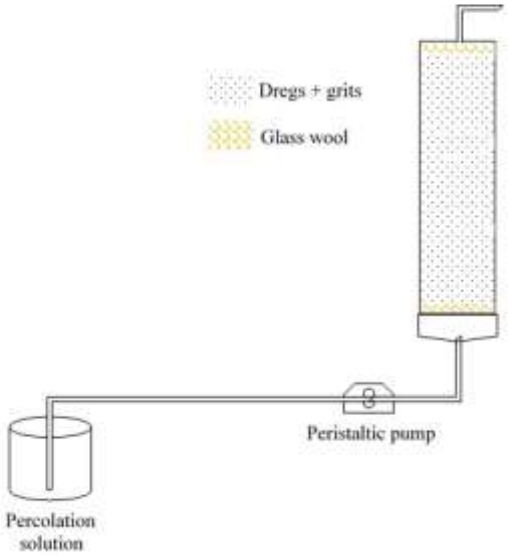

Figure 2. Adsorption column tests (scheme).

2.4. PREPARATION OF THE PERCOLATION SOLUTION (ADSORBATE)

The percolate solution was formulated with Cu, and SO_4 and distilled water (Han et al. 2016), with concentrations of 600 and 4,300 mg/L, respectively. The parameters and respective concentrations were determined based on values usually found for ADM (Fernando et al., 2018, Vital et al., 2018).

2.5. ADSORPTION KINETICS

The adsorption kinetics were assessed over a period of 180 min, by taking samples at 5, 10, 20, 30, 60, 90 and 180 min. The suspension of 2 g : 20 mL of the adsorbent material was maintained under stirring in a solution of distilled water prepared with 600 mg/L of Cu and 4,300 mg/L of SO_4. The pH of the solution was 2.5, according to the common conditions in acid drainage in mines (Table 1), and the agitation was carried out at 100 rpm. Two tests were carried out: in the first the pH was maintained bellow 2.5 by adding nitric acid and in the second the pH was not controlled. Then, the removal efficiencies of Cu and sulfate was determined in two stirring interval and different S:L ratios.

2.6. COLUMNS TEST

The column experiments was carried out in continuous upflow (Shabalala et al. 2017; Quina, 2005), with the use of a peristaltic pump, and the contact interval between solid and liquid (30 min) determined from the adsorption kinetics test, with 20 g of adsorbent material and 200 mL of Cu and SO_4 solution. The initial pH of solution was 2.5 for both columns. The evaluated parameters were Cu and SO_4 concentrations, commonly found in acid drainage in copper mining (Table 1).

2.7. ANALYTICAL METHOD

The final concentrations of Cu present in the solution percolated through the adsorbent medium was determined by energy dispersive X-ray fluorescent (EDXRF), using a NEX CG Rigaku Spectrometer, according to ASTM D4927. For sulfate determination the titration method was used with torina indicator solution, precipitating of barium chloride in barium sulfate (Marques, 2013).

3. RESULTS AND DISCUSSION

3.1. Characterization of adsorption materials

The concentration of calcium oxide in kraft pulp mill dregs used in this study is within the typical values, 30 - 44% in dregs samples from a pulp mill in Northern Sweden (Table 3). Some variations are due to the efficiency of the liquor recovery process or to the origin of the processed wood (Makitalo et al. 2014). Calcium, Mg, Na, Fe, S, Mn, Si, Al, K and P are the main inorganic elements presents on dry dregs (Martins et al. 2007).

Table 3. Elemental content measured on *dregs* and *grits.*

ELEMENT	**DREGS (mg/kg)**		**GRITS (mg/kg)**	
	Measured	[1]	Measured	[2]
CaO (%)	42.5	30 - 44	54.2	69.0
SiO_2	0.81	1.3	0.3	-
SO_3	0.75	1.4	0.14	1.4
MgO	4.99	3.3	0.59	-
Fe_2O_3	0.17	0.8	0.05	-
K_2O	0.07	0.28	0.02	1.4
Al_2O_3	0.4	0.43	0.19	-
Cl	0.01	0.1	0.004	-
P_2O_5	0.71	3.3	0.28	-
Na	*14,700	19,800 – 71,000	*13,200	10,400
Ca	304,500	175,000 – 388,500	388,500	417,000

[1]Makitalo et al. 2016; [2]Cabral et al. 2008; *Determined by Energy-dispersive X-ray spectroscopy (EDX) on SHIMAZU's EDX 1300 micro model spectrometer

The metal concentrations are bellow or within the typical values (Table 4), and it has like characteristic, low solubility in water (Golmaei et al., 2018). The source of metals and others inorganic elements on dregs and grits is associate to it absorption on soil, by plants roots, and fixed in the wood, on chemicals used on chips cooking process, in the water, and corrosion product of the equipment (Manskinen et al., 2011).

Table 4. Metals presents in *dregs* and *grits*

ELEMENT	**DREGS (mg/kg)**					**GRITS (mg/kg)**	
	Measured	[1]	[2]	[3]	[4]	Measured	[5]
Cd	ND	5.2	4.5	9.4	11	ND	4.75
Cr	15.3	56	39	118	160	0.54	12.4
Cu	54.95	81	129	102	330	16.3	4.6
Ni	32.5	189	175	84	80	ND	25
Pb	17.35	47	45	13	52	6.29	34
Zn	88	160	242	1,000	6,490	7.19	15

[1,5]Cabral et al. 2008; [2]Modolo et al. 2010; [3]Kinnarinen et al. 2016; [4]Makela et al. 2016; ND: Not Detected

The total porosity of dregs and grits were 66% and 42%, respectively (Table 5). Porosities higher than 70% was found for dregs generated in a Swedish pulp mill (Makitalo et al. 2014). The high porosity of the material has a direct positive relation with the removal of contaminants in an aqueous media, by intra-particle diffusion phenomenon (Singh et al., 2018; Zhou et al., 2018).

The size and homogeneity of the adsorbent particles are important to the best performance of PRB (Sulaymon et al. 2015). The plastic characteristic and low permeability of the dregs, suggests their mixing with other material (Makitalo et al. 2014), to prevent the contamination plume from encountering a preferential flow of higher permeability outside the reactive barrier, a situation observed for the use of zero-valent iron as the only adsorbent medium (Han et al. 2016; Calabrò et al. 2012). The sintering mechanism can be used to adjust the particle size of adsorbent materials with their agglutination by the action of the temperature below the melting point (Borgwardt, 1989).

Table 5. Physical and chemical characterization of dregs and grits

PARAMETERS	DREGS				GRITS		
	Measured	[1]	[3]	[4]	Measured	[2]	[3]
Moisture (%)	31	48 - 65	-	-	6.5	-	16
pH	10.53	10 - 11	-	-	10.26	12 - 13	13
EC (mS/cm)	4.3	-	-	2.5	0.193	-	-
VS (%)	3.5	-	8.3	-	0.17	-	2.4
Bulk density (g/cm^3)	0.61	0.67	-	0.44	1.26	-	-
Porosity (%)	66	73 - 82	-	-	42	-	-

[1]Makitalo et al. 2014; [2]Cabral et al. 2008; [3]Modolo et al. 2010; [4]Pasandín et al. 2016

Acid neutralization capacity

Dregs and grits showed similar behavior regarding their acid neutralization capacity, notably for pH smaller to 8 (Figure 3), with a major consumption of H^+ between pH 6 and 5, suggesting the influence of alkalinity by carbonates (EPA, 2006). For similar study with dregs in Sweden, the major consumption of H^+, in the pH 8 interval, suggest the same influence like alkalinity source (Makitalo et al. 2014).

The high buffer capacity of the dregs is well known (Zambrano et al. 2010), and it was studied as an alternative liming material on soil (Cabral e al. 2008; Jordan and Rodriguez, 2004). The maintenance of the dregs alkalinity condition used as remediation of acid mine drainage in a long term, suggests a good potential to this application (Makitalo et al. 2016). Alkaline composts such as carbonate and hydroxides in dregs and grits (Golmaei et al. 2018; Manskinen et al. 2011; Cabral et al. 2008; EPA, 2006), react with hydrogen ion, neutralizing or increasing the pH of the solution and removing metals by precipitation mechanisms (Torres et al. 2018; Gray et al. 2006).

According to the assay, dregs and grits have an acidity neutralization capacity with potential for Cu precipitation, until 15 mmol H^+ per gram.

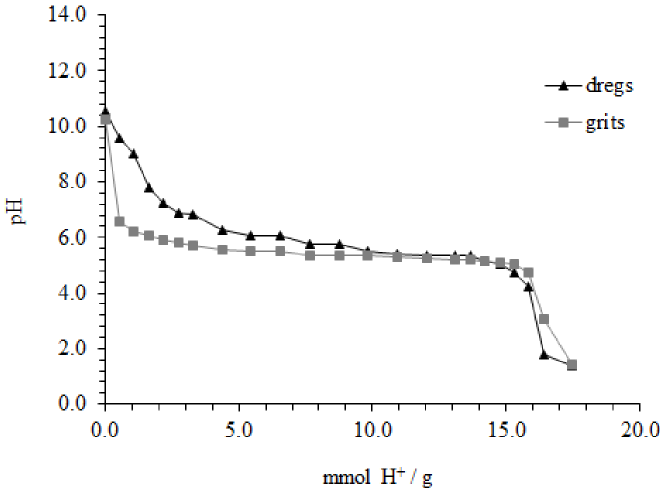

Figure 3. Acid neutralization capacity of dregs and grits.

3.2. Adsorption Kinetics

It was verified, in the first kinetic assay, the maximum retention of 63% (dregs) and 80% (grits) for Cu and 79% (dregs) and 89% (grits) for SO_4. The maximum retention for Cu occurred at 5 min with dregs and 180 min with grits. The maximum retention for SO_4 occurred at 60 min for dregs and 90 min for grits (Figure 5).

On the second kinetic assay, it was identified 99.5% retention of Cu at 5 min using dregs, without pH control (alkaline pH). A significant Cu retention with grits initiated after 60 min and at 180 min achieved a 97% removal. The fast and high retention of the Cu by dregs suggest its precipitation in $Cu(OH)_2$, common in alkaline conditions (Fu and Wang, 2011). A sulfate retention of 28% using both materials was achieved during the second kinetic assay. The initial concentrations of Cu and SO_4 was 600 mg/L and 4,300 mg/L, respectively. Both precipitation and adsorption mechanisms seems to have an important role according to these results.

There was a maximum adsorption for Ni and Cu in 5 min and 15 min, respectively, using MgO as adsorbent material (Feng et al. 2018; Madzokere and Karthigeyan, 2017). The higher Cu retention for a synthetic solution with initial concentration of 400 mg/L was at 30 min, in adsorption kinetics test, using calcium silicate powder as adsorption material (Ma et al. 2018).

For synthetic solution of sulfate with initial concentration of 1,800 mg/L and pH 4.5, retention high than 85% occurred at 10 min, in adsorption kinetics test, using $AlCl_3$ as adsorbent material, by co-precipitation mechanism (Silva et al. 2010). The selective precipitation of copper occurs on a pH range of 2.8 – 4.71 and increases over time (Zhou et al. 2018). It was verified a similar precipitation mechanism using a molar rate 1:1 of calcium carbonate and Cu, presenting more than 99% Cu removal (Hu et al. 2017).

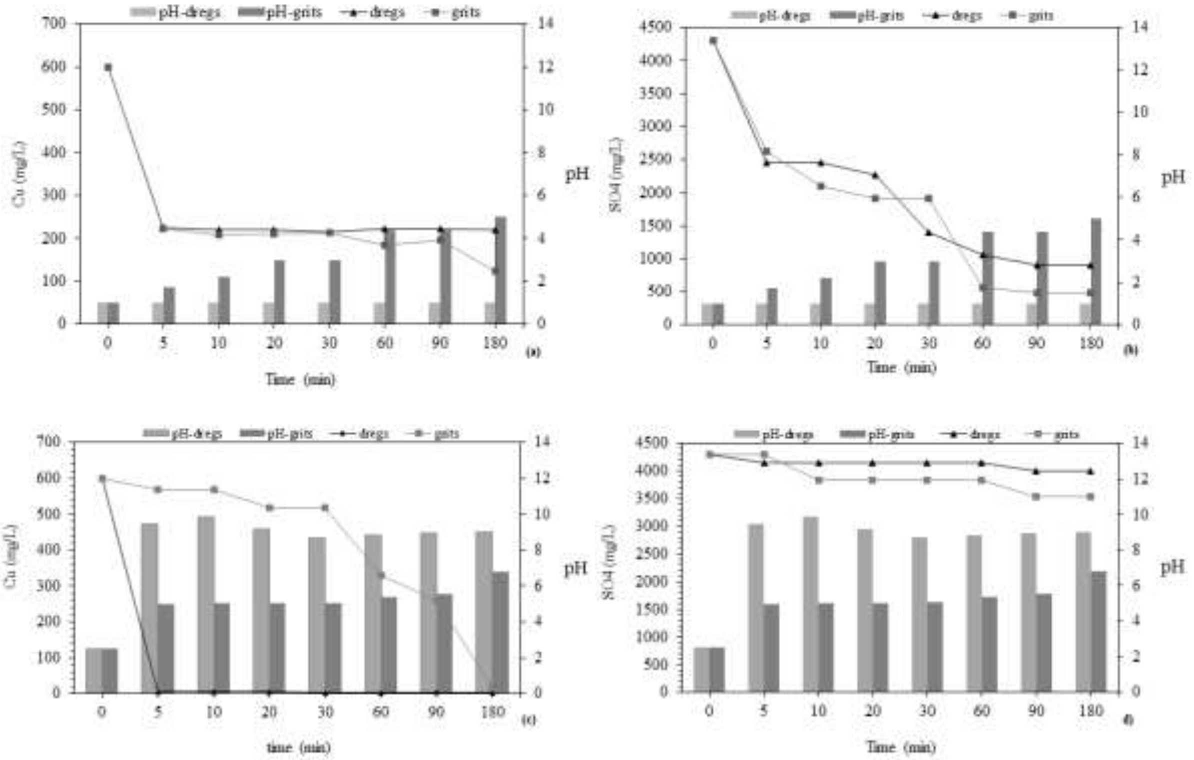

Figure 5. Adsorption kinetic of Cu and SO_4 with pH control (a) (b) and without pH control (c) (d) by dregs and grits

A high buffer capacity was verified for both adsorption materials, notably for dregs. The pH was approximately 10 until S:L ratio of 1:100. For a S:L ratio of 1:1000, the pH was always above 7 (Figure 6a). In this pH condition, the Cu ion precipitates (Zhou et al. 2018), as showed in the Figure 5c. A significant decrease of the pH for the dregs batch adsorption test was verified after 1:100 (S:L), but the values was similar for assays of 3h and 24h, differently of grits comportment (Figure 6b). Chemical precipitation is a mechanism traditionally used for metal removal in acid mine drainage (Matlock et al. 2002), but this technique has been questioned due to the high amount alkali needed, such as limestone (Jafaripour et al. 2015), justifying the use of the alternative material, such as the industry wastes dregs and grits, due at large availability and low cost.

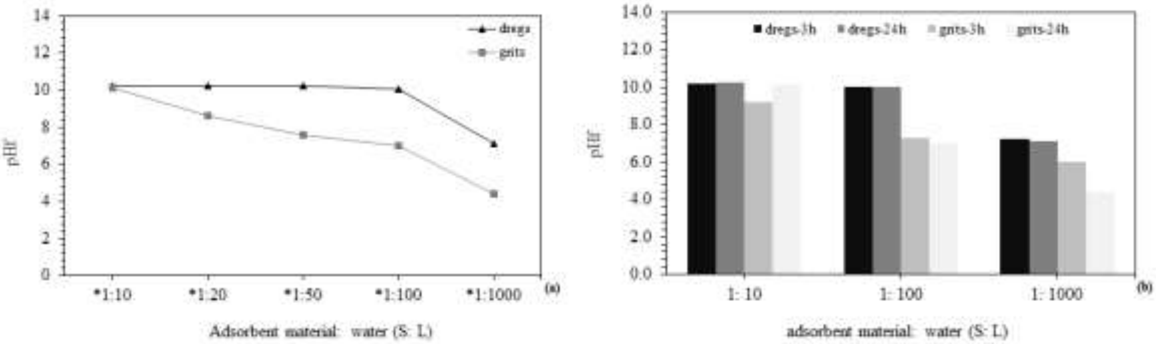

Figure 6. Buffer capacity of adsorption materials: (a) time: 3h; (b) time: 3h and 24h

3.3. Adsorption batch test

During the adsorption batch tests, the retention of Cu was 99% and 97% for dregs and grits, respectively, for a S:L ratio up to 1:10. After increasing the S:L ratio to 1:100, the Cu retention was reduced, especially for grits, showing only a 3% efficiency, remaining similar for the other S:L ratios. The Cu removal for dregs was 75% up to S:L ratio of 1:100, decreasing to 27% at 1:500 ratio (Figure 7). The Cu removal decreases as the pH decreases, suggesting that precipitation is a main mechanism of removal.

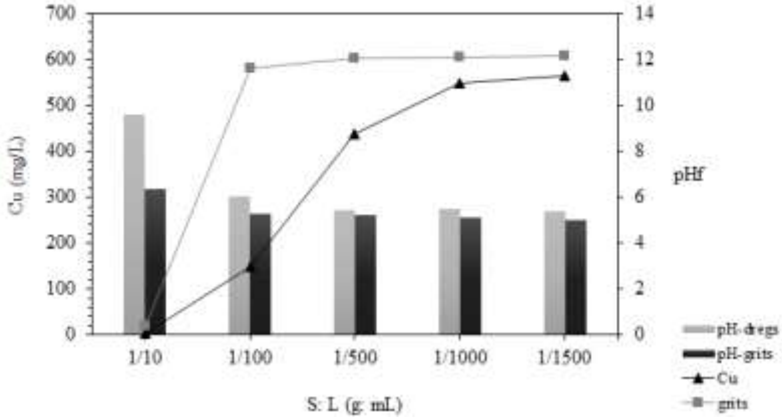

Figure 7. Copper adsorption for dregs and grits in different rates S: L

The initial sulfate concentration was 4.300 mg/L, and an average retention efficiency of 5% for dregs and grits was obtained (Figure 8).

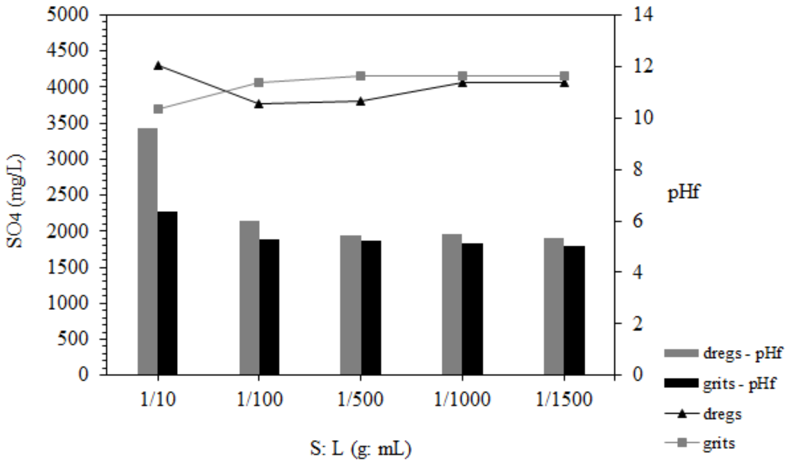

Figure 8. Sulfate removed for different rates solid: liquid

3.4. Adsorption column tests

The Cu retention in the adsorption column test was 99%, 82% and 56% using dregs with S:L ratio of 1:10, 1:20 and 1:50, respectively. For grits, these values were 26%, 24% and 7% for the same ratios, respectively (Figure 9a). The sulfate removal was below 6% for all adsorption materials and S:L ratios (Figure 9b). The high Cu removal was verified for alkaline pH, suggesting the precipitation mechanism. It suggests a consumption of 1 t of material per cubic meter of acid mine drainage (AMD). Such as an abandoned gold and silver mine in Japan, with an AMD flow of 18,000 m^3 / year (Yamaguchi et al., 2015), it would be necessary 1,800 t of dregs or grits. The mining activity in Minas Gerais State, Brazil, has a capacity for generating until 104 billions tones per year, with US$ 26 millions of costs using commercial limestone to AMD remediation (Mello et al., 2006). This value represents an economy generated with use industries waste, such as dregs and grits, for this purpose. The rare lands recovery, present on the precipitate, it can be obtained by solvent extraction, electrowinning, cementation or precipitation, it is an opportunity that adds value to permeable reactive barrier, and it should be studied.

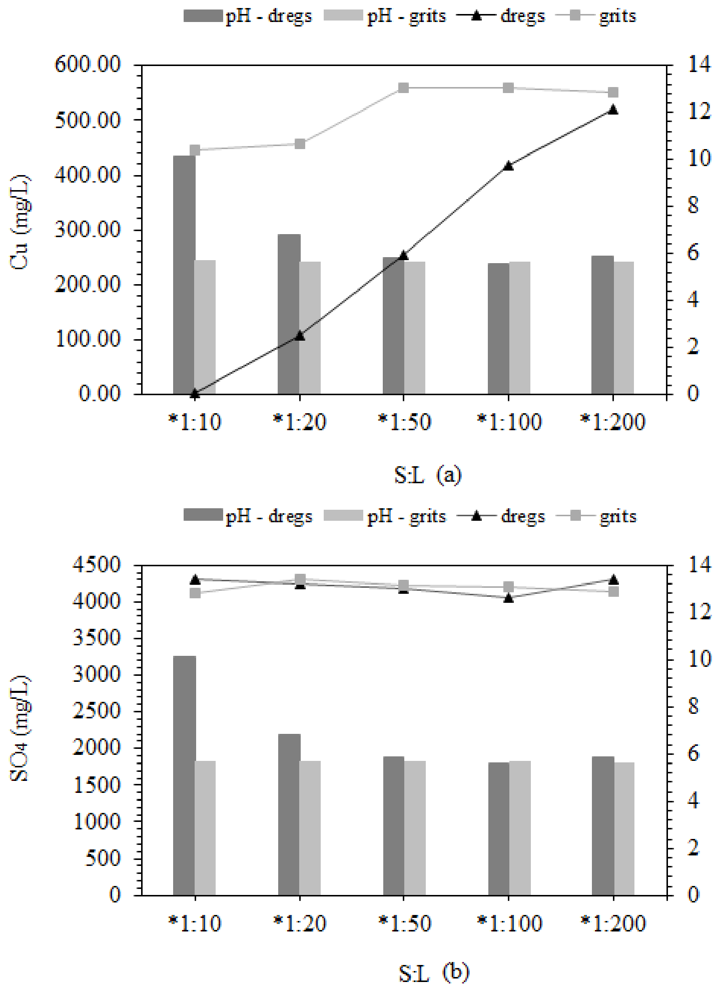

Figure 9. Cooper (a) and sulfate (b) remove in columns filled with dregs and grits

Point of zero charge

The pH_{PZC} was 11.5 and 12 for dregs and grits, respectively (Figure 4), predicting that the surface of adsorbent media should have a positive charge, attracting anionic ions (Soares et al. 2016; Cerovic et al. 2007). This condition suggests a potential sulfate adsorption, such as presented in Figure 5b, where more than 80% sulfate removal was achieved, by other mechanisms, such as precipitation and ionic exchange (Silva et al. 2010). High points of zero charge (8.5 - 11) due to the presence of $CaCO_3$ in dregs and grits are reported (Kosmulski, 2009). The knowledge of the surface charge is important to select the adsorption materials, according to the removal of desired contaminants (Vieira et al. 2009). The use of sequential permeable reactive barriers can be an interesting option to, simultaneously, remove anionic and cationic ions in aqueous media, each one using a material with different pH_{PZC} (Holmes et al., 2017; Han et al., 2016).

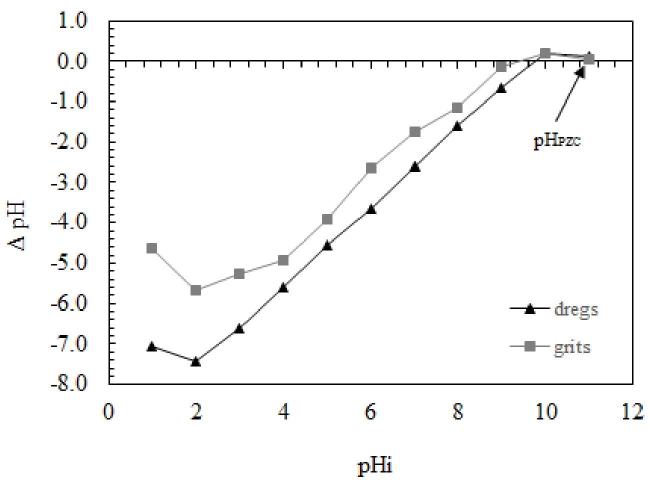

Figure 4. Determination of pH_{PZC} for dregs and grits

4. CONCLUSIONS

Dregs and grits showed a potential to be used as permeable reactive barrier for Cu removal. The main Cu removal mechanism was chemical precipitation, notably for the S:L ratio 1:10, when a removal above 99% was obtained.

The sulfate removal efficiency occurred at pH bellow 5, demanding about 18 mmol H^+ (HCl) per gram of dregs and grits.

Dregs and grits has potential for metals removal in another industrial effluents, such as tubular furniture and tannery industry, being necessary complementary studies to evaluation specific concentration and multi-elmentars compositions.

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CONCLUSÕES E RECOMENDAÇÕES FINAIS

A substituição do solo pelo composto de dregs+grits ou pela lama de cal, como material de cobertura intermediária em aterros sanitários, apresenta ganhos econômicos e ambientais para o setor de polpa celulósica e para a administração pública, notadamente os municípios.

Com base nos parâmetros avaliados, a lama de cal não influenciou negativamente a dinâmica biológica do aterro sanitário experimental, notadamente pelo monitoramento da demanda química de oxigênio (DQO). O composto de dregs+grits influenciou na cinética de estabilização da matéria orgânica, demandando um maior intervalo de tempo para a estabilização dos resíduos orgânicos. No entanto, o resultado final foi semelhante aos aterros com cobertura de lama de cal e com solo. Considerando que um aterro sanitário tem vida útil mínima de 20 anos, e que permanece biologicamente ativo por várias décadas após seu encerramento, entende-se que não haverá influência significativa em aterros urbanos.

O tratamento biológico dos chorumes gerados nas unidades experimentais com lama de cal, dregs+grits e com solo (controle) apresentaram resultados satisfatórios, com eficiências acima de 80% para remoção de DQO, sugerindo potencial de uso desses materiais. O chorume formado na unidade experimental com dregs+grits, no entanto, necessitou de adição de ácido (H_2SO_4) para a manutenção do pH adequado no reator biológico.

As colunas preenchidas com composto de dregs+grits e a lama de cal apresentaram eficiências de remoção de metais semelhantes ao solo, exceto para o Cu, tendo ocorrido dessorção deste íon nas colunas preenchidas com dregs+grits.

A eficiência de remoção de Cu em drenagem ácida da mineração com o uso de dregs variou de 63% a 99,5%, em pH ácido e alcalino, respectivamente, com relação sólido: líquido de até 1:100. O grits apresentou eficiência similar até a relação 1:10.

A remoção de sulfato por dregs e grits em águas de drenagem ácida mostrou-se eficaz em condições ácidas ($pH < 4,5$), demandando excessivo consumo de ácido, o que pode inviabilizar o uso destes materiais para o fim proposto. Sugere-se ensaios como barreiras sequenciais, onde a primeira barreira possa tornar o pH ácido, removendo sulfato por precipitação, em sulfato de sódio por exemplo, e na sequência uma barreira com dregs, onde o filtrado da primeira barreira possa assumir características alcalinas, e ser precipitado/adsorvido nesta, permitindo assim o tratamento concomitante do sulfato e do cobre.