UNIVERSIDADE ESTADUAL DE MARINGÁ
CENTRO DE TECNOLOGIA
DEPARTAMENTO DE ENGENHARIA QUÍMICA
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

INVESTIGAÇÃO DA TOXICIDADE E FORMAÇÃO DE SUBPRODUTOS NO TRATAMENTO DE LIXIVIADO DE ATERRO SANITÁRIO POR PROCESSO FOTO-ELETRO-FENTON INTEGRADO A OXIDAÇÃO BIOLÓGICA

Daiana Seibert
Engª Ambiental, UFFS, 2016
Mestre em Ambiente e Tecnologias Sustentáveis, UFFS, 2017
Orientadora: Profª. Drª. Rosângela Bergamasco
Coorientador: Prof. Dr. Fernando Henrique Borba

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COMISSÃO JULGADORA

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Profª. Drª. Rosângela Bergamasco
Orientadora

Fernando Henrique Borba.

Prof. Dr. Fernando Henrique Borba
Coorientador

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Membro

Quelen Letícia Shimabuku Biadola

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Membro

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Drª. Natália Cândido Homem - DTx/Uminho
Membro

Aline T. A. Baptista

Profª. Drª. Aline Takaoka Baptista - DAAEQ/UTFPR
Membro

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INVESTIGAÇÃO DA TOXICIDADE E FORMAÇÃO DE SUBPRODUTOS NO TRATAMENTO DE LIXIVIADO DE ATERRO SANITÁRIO POR PROCESSO FOTO-ELETRO-FENTON INTEGRADO A OXIDAÇÃO BIOLÓGICA

AUTOR: DAIANA SEIBERT
ORIENTADOR: PROFª Drª. ROSÂNGELA BERGAMASCO
COORIENTADOR: PROF. Dr. FERNANDO HENRIQUE BORBA

Tese de Doutorado; Programa de Pós-Graduação em Engenharia Química; Universidade Estadual de Maringá; Av. Colombo, 5790, BL E46 – 09; CEP: 87020-900 – Maringá – PR, Brasil, defendida em 18 de agosto de 2022. 171 p.

RESUMO

A disposição de resíduos sólidos urbanos em aterros sanitários é uma técnica muito utilizada e considerada ambientalmente correta em países em desenvolvimento. Contudo, esta prática leva a geração de efluentes líquidos, que carreados pelas águas pluviais originam o Lixiviado de Aterro Sanitário (LAS). O LAS pode apresentar características muito variadas, como consequência das características dos resíduos dispostos, condições climáticas e geográficas. Recentemente a ascensão de novas técnicas analíticas, tem direcionado a atenção de pesquisadores acerca da identificação de contaminantes de preocupação emergente (CPE) no LAS, destacando-se os chamados químicos desreguladores endócrinos, do inglês: *Endocrine Disrupting Chemicals (EDCs)*, o que dificulta seu tratamento através de técnicas convencionais. Uma revisão bibliográfica foi realizada e constatou que bisfenol-A (BPA), ftalatos (PAEs), e surfactantes estavam entre os 12 EDCs mais frequentemente detectados em LAS. Processos de Eletro Oxidação Avançada apresentam-se como uma alternativa promissora para degradação e mineralização de LAS, bem como dos CPE presentes nesta complexa matriz ambiental. Portanto, o presente trabalho investigou as condições operacionais adequadas para a aplicação do Processo Foto-Eletro-Fenton ao tratamento de LAS, empregando eletrodos de ferro como cátodo e ânodo, bem como o estudo da melhor estratégia de integração do processo FEF a um tratamento baseado em oxidação biológica. Através das seguintes condições operacionais: 9000 mg H_2O_2 L^{-1}; 60 mg Fe L^{-1}; I=2,3 A; pH entre: 3,5-4,5; injeção de O_2 a taxa de 3,2 L O_2 min^{-1} e 45 min de reação, foi possível reduzir os níveis de toxicidade e geração de subprodutos as amostras tratadas de LAS, aumentar sua fração de biodegradabilidade (DBO_5/DQO=0,40), e possibilitar uma posterior integração com sistema de oxidação biológica, sendo esta a melhor estratégia de integração para o tratamento do LAS (FEF 45 min. + Bio 24 h).

Palavras chave*:* Combinação de processos; Processo de Eletro Oxidação Avançada; Tratamento de Efluentes.

STUDY OF TOXICITY AND BYPRODUCTS FORMATION FROM LANDFILL LEACHATE TREATMENT BY PHOTO-ELECTRO FENTON PROCESS INTEGRATED WITH BIOLOGICAL OXIDATION

AUTHOR: DAIANA SEIBERT
SUPERVISOR: PROFª Drª. ROSÂNGELA BERGAMASCO
COSUPERVISOR: PROF. Dr. FERNANDO HENRIQUE BORBA

Doctoral Thesis; Chemical Engineering Graduate Program; State University of Maringá; Av. Colombo, 5790, BL E46 – 09; CEP: 87020-900 – Maringá – PR, Brazil, presented on 18th August 2022. 171 p.

ABSTRACT

The disposal of urban solid waste in sanitary landfill is a common and acceptable technique employed in developing countries. However, this practice originates a liquid waste that is carried by rain water, generating the sanitary landfill leachate (SLL). The SLL may present different characteristics, according to the wastes disposed, geographic and climatic conditions. Recently, the improvement of analytical techniques has directed the attention of researches to the identification of contaminants of emerging concern (CEC) in SLL, highlighting the Endocrine Disrupting Chemicals (EDCs), impairing the application of conventional wastewater treatment techniques. A review from the literature reported that bisphenol-A, phthalates and surfactants were between the 12 main frequently EDCs detected in SLL. Advance Electrochemical Advanced Oxidation Process (EAOPs) are considered a suitable treatment alternative to remove and mineralize the organic load, as well as CEC from this complex environmental matrix. Therefore, the present work investigated the adequate operational conditions for the Photo-Electro-Fenton (PEF) process employed to SLL treatment, using iron electrodes as cathode and anode, as well as the best combination strategy with biological oxidation. With the application of the following operational conditions 9000 mg H_2O_2 L^{-1}; 60 mg Fe L^{-1}; I=2,3 A; pH: 3,5-4,5; O_2 injection rate 3,2 L O_2 min^{-1} and 45 min of reaction, it was possible to reduce the amount of by-products generated and the toxicity levels from the SLL treated samples, increase the biodegradability index (BOD_5/COD=0,40), and make possible the post-biological treatment, being this the best treatment strategy (PEF 45 min. + Bio 24 h).

Keywords: Combined Process; Electrochemical Advanced Oxidation Process; Wastewater Treatment.

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ARTIGO 1

METODOLOGIA EXPERIMENTAL

ARTIGO 2

NOMENCLATURA OU LISTA DE SÍMBOLOS

•OH – radicais hidroxila

BBP - Butil benzil ftalato, do inglês: *Butyl benzyl phthalate*

BDD – Diamante dopado com boro, do inglês: *boron doped Diamond*

BPA – Bisfenol A, do inglês: *Bisphenol A*

CG-MS - Cromatografia gasosa acoplada ao espectro de massas

CL$_{50}$ – Concentração letal que causa mortalidade em cinquenta por cento (50%) da população exposta

CT – Carbono total

DBO$_5$ – Demanda bioquímica de oxigênio em 5 dias

DBO$_5$/DQO – Fração de biodegradabilidade

DBP – Dibutiloftalato, do inglês: *Dibutyl phthalate*

DCCR – Delineamento composto central rotacional

DEHP – Di-(2-etilhexil)ftalato, do inglês*: Di-(2-ethylhexyl)phthalate*

DEP - Ftalato de dietila, do inglês*: Diethyl phthalate*

DiBP – Di-isobutiloftalato, do inglês: *Diisobutyl phthalate*

DIDP – Diisodeciloftalato, do inglês: *Diisodecyl phthalate*

DINP – Diisononilaftalato, do inglês: *Diisononyl phthalate*

DIOP – Diiso-octiloftalato, do inglês: *Diisooctyl phthalate*

DOP - Dioctil ftalato, do inglês: *Dioctyl phthalate*

DMP - Ftalato de dimetila, do inglês: *Dimethyl phthalate*

DnBP – Di-n-butiloftalato, do inglês: *Di-n-butyl phthalate*

DnHP – Di-n-hexiloftalato, do inglês: *Di-n-hexyl phthalate*

DTBP - 4-terc-butilfenol, do inglês: *4-tert-butylphenol*

DQO – Demanda química de oxigênio

EDCs – Químicos desreguladores endócrinos, do inglês: *Endocrine Disrupting Chemicals*

EF – Eletro Fenton

FEF – Foto-eletro Fenton

HMWPE – Ftalatos de elevado peso molecular, do inglês: *High Molecular Weight Phthalates*

LAS – Lixiviado de aterro sanitário

MSR – Metodologia de superfície de resposta

NP – Nonilfenol, do inglês: *Nonylphenol*

NT – Nitrogênio total

PAEs – Ésteres de ácido ftálico, do inglês: *Phthalic acid esters*

PEOAs – Processos de eletro-oxidação avançada

PF – Processo Fenton

PFF – Processo foto-Fenton

POAs – Processos de oxidação avançada

SF – Sólidos fixos

SS – Sólidos suspensos

ST – Sólidos totais

SV – Sólidos voláteis

TAIC – Isocianurato de trialilo, do inglês: *Triallyl isocyanurate*

UV_{254nm} - Compostos aromáticos com absorção no comprimento de onda de 254 nm

4OP - 4-octilfenol, do inglês: *4-Octylphenol*

SUMÁRIO

APRESENTAÇÃO

Em consonância com a Resolução nº 030/2022-PEQ, a presente tese de doutorado está dividida em dois artigos científicos previamente publicados. Além da apresentação dos artigos em sua forma original, a tese também conta com uma introdução, objetivos, revisão bibliográfica, e conclusão geral.

O primeiro artigo intitulado “Presence of endocrine disrupting chemicals in sanitary landfill leachate, its treatment and degradation by Fenton based processes: A review”, foi publicado na revista Process Safety and Environmental Protection (ISSN: 0957-5820, Fator de impacto: 7,926 e Qualis A1) em setembro de 2019. https://doi.org/10.1016/j.psep.2019.09.022.

O segundo artigo intitulado “Two-stage integrated system photo-electro-Fenton and biological oxidation process assessment of sanitary landfll leachate treatment: An intermediate products study”, foi publicado na revista Journal of Environmental Chemical Engineering (ISSN: 1385-8947, Fator de impacto: 16,744 e Qualis A1) em abril de 2019. https://doi.org/10.1016/j.cej.2019.04.162.

Os dois artigos são resultado do projeto de pesquisa de doutorado intitulado “Aplicação de processos eletro-oxidativos avançados (PEOAs) no tratamento de lixiviado de aterro sanitário” e serão utilizados como parte dos requisitos necessários à obtenção do Grau de Doutora em Engenharia Química, área de Desenvolvimento de Processos.

1. INTRODUÇÃO

Mudanças na sociedade, tais como rápida urbanização e crescimento populacional tem emergido a disposição de resíduos sólidos como um problema de gestão ambiental (GHOSH; THAKUR; KAUSHIK, 2017). Mesmo que aterros sanitários apresentem algumas evoluções tecnológicas como o controle e tratamento de gases e efluentes, a disposição de resíduos sólidos em aterros sanitários não é a melhor solução do ponto de vista ambiental, contudo ainda é a mais praticada e indicada em países em desenvolvimento (COSSU, 2010; JURCZYK; KOC-JURCZYK, 2017).

Como resultado da degradação físico-química e biológica dos resíduos sólidos urbanos dispostos nas células dos aterros sanitários é produzido o chorume, que carreado pelas águas pluviais origina o lixiviado de aterro sanitário (LAS) (CHEMLAL et al., 2014; GHOSH; THAKUR; KAUSHIK, 2017; RENOU et al., 2008). Este líquido é composto de uma variedade de produtos químicos que são o resultado da passagem de água através da massa de resíduos, saturando-os com matéria orgânica e inorgânica. Desta maneira, os LAS apresentam desafios significativos para o seu descarte/tratamento em aterros operadores em todo o mundo, principalmente devido ao seu potencial para contaminar solos, águas superficiais, aquíferos e água do mar (KHALIL et al., 2018).

Geralmente LAS são tratados por processos de oxidação biológica (EL-GOHARY; KAMEL, 2016, p.; ROBINSON, 2017). Entretanto, os LAS podem apresentar diferentes características, especialmente os LAS maduros, que apresentam elevada concentração de amônia e substâncias não biodegradáveis devido à fase metanogênica de degradação dos resíduos aterrados, em que ocorrem processos anaeróbios (ABD EL-SALAM; I. ABU-ZUID, 2015; KJELDSEN et al., 2002; MCBEAN, E. A.; ROVERS, F. A.; FARQUHAR, G. J., 1995; MÜLLER et al., 2015; RENOU et al., 2008), tornando difícil a manutenção das comunidades microbianas para aplicação de tratamentos biológicos (JURCZYK; KOC-JURCZYK, 2017).

A idade do aterro sanitário também é um fator que pode ser levado em consideração quando se trata das condições de biodegradabilidade dos LAS. LAS jovens (DBO_5/DQO>0,6) podem ser tratados por técnicas biológicas, visto que estes apresentam compostos biodegradáveis. Por outro lado, LAS maduros ($DBO_5/DQO<0,3$) apresentam em sua composição grandes concentrações de compostos orgânicos de elevada massa molecular, desta forma, técnicas de tratamento físico-químicas são as mais indicadas para seu tratamento (BAIJU et al., 2018; GAO et al., 2015; KURNIAWAN; LO; CHAN, 2006; RENOU et al., 2008).

Dentre as técnicas físico-químicas aplicadas ao tratamento de LAS, o estudo de processos oxidativos avançados (POAs) (GHANBARZADEH LAK et al., 2018; SEIBERT et al., 2017; WANG et al., 2018) e eletro-oxidativos avançados (PEOAs) (DE PAULI et al., 2017, 2018; FERNANDES et al., 2017; FUDALA-KSIAZEK et al., 2018, 2018) para o tratamento de LAS estão se difundindo no meio científico, trazendo bons resultados para a remoção de matéria orgânica refratária. Dentre os PEOAs, destaca-se o processo foto-eletro-Fenton (FEF), que é baseado na reação de Fenton onde uma transferência de elétrons entre peróxido de hidrogênio (H_2O_2) e um íon metálico (Fe^{2+}) tem como objetivo a produção de radicais hidroxila ($^{\bullet}OH$) em meio ácido (FENTON, 1894; UMAR; AZIZ; YUSOFF, 2010). Nos processos eletro-oxidativos, tais como EF e FEF, a oxidação dos poluentes ocorre através de uma oxidação eletroquímica indireta, em que $^{\bullet}OH$ são produzidos a partir da reação de Fenton, e os reagentes (H_2O_2 e Fe^{2+}) são eletrogerados *in situ* (DENG; ENGLEHARDT, 2006). Este processo pode ser melhorado com a assistência de luz, uma vez que neste caso a fotólise de H_2O_2 produz $^{\bullet}OH$ extra e espécies fotoativas de ferro participam na remoção de poluentes (DENG; ENGLEHARDT, 2006; MONTEIL et al., 2018; RADHA; SIRISHA, 2018). Assim, processos de oxidação eletroquímica podem levar a remoção de íons inorgânicos e mineralização de compostos orgânicos refratários (FERNANDES et al., 2015; MANDAL; DUBEY; GUPTA, 2017). PELLENZ et al. (2020) reportou que o processo de FEF foi eficiente para a remoção de poluentes emergentes, bem como remoção de carga orgânica de LAS. De acordo com a revisão realizada por SEIBERT et al. (2020), dentre diferentes técnicas de PEOAs empregadas para o tratamento de águas e efluentes, o processo FEF se destacou, como uma das técnicas mais eficientes para remoção e oxidação de contaminantes presentes em fase aquosa.

Embora estes processos sejam descritos como técnicas que apresentam elevadas eficiências de remoção, a permanência de subprodutos de reação após o tratamento ainda é uma preocupação. Dentre os compostos que persistiram ao tratamento convencional, bisfenol A (BPA) foi identificado por alguns autores (BADERNA et al., 2011; REIS et al., 2017). BPA é um químico industrial empregado na produção de plásticos de policarbonato e resinas epóxi, sendo conhecido por provocar respostas celulares por ligação a receptores nucleares de estrogênio (BERONIUS et al., 2010). Além de BPA, outros compostos classificados como químicos desreguladores endócrinos (EDCs) (US. ENVIRONMENTAL PROTECTION AGENCY–USEPA, 2012) foram identificados em LAS e caracterizados como poluentes persistentes aos tratamentos convencionais comumente aplicados a este efluente (BADERNA et al., 2011; KHALIL et al., 2018; QI et al., 2018; RODGERS; RUDEL; JUST, 2014; SEIBERT et al., 2019b; YI et al., 2017).

Com o objetivo de melhorar a remoção de poluentes persistentes e reduzir a formação de subprodutos em amostras de LAS tratado, métodos de tratamento multi-estágio têm sido estudados (BAIJU et al., 2018; DE PAULI et al., 2018; MOROZESK et al., 2017; POBLETE et al., 2017). Como LAS geralmente apresentam baixa biodegradabilidade, e em virtude disso, tratamentos convencionais não se mostram totalmente eficientes, uma alternativa é a aplicação de métodos de oxidação química como pré-tratamentos visando à conversão da matéria orgânica recalcitrante inicial em compostos orgânicos intermediários mais biodegradáveis ou a aplicação de processos de oxidação química como pós-tratamento para processos biológicos (DE MORAIS; ZAMORA, 2005; EL-GOHARY; KAMEL, 2016; FERNANDES et al., 2014; NTAMPOU; ZOUBOULIS; SAMARAS, 2006; SICILIANO; RUGGIERO; DE ROSA, 2013).

Desta forma, o objetivo deste trabalho compreende definir através de uma metodologia de superfície de resposta a condição ótima do processo FEF na redução da concentração inicial de carbono total (CT), visando melhorar a fração de biodegradabilidade do LAS a fim de acoplar em um sistema de oxidação biológica (Bio). A melhor estratégia de integração e um estudo dos subprodutos gerados após cada etapa de tratamento foi realizada, bem como a investigação das condições de toxicidade das amostras brutas e tratadas. Uma revisão bibliográfica também foi realizada com o objetivo de identificar os principais contaminantes de preocupação emergente identificados em LAS. Sendo assim, a seção de resultados da presente tese foi subdividida em capítulos apresentando os artigos previamente publicados. Além disso, na seção de apêndices encontra-se o artigo que foi redigido como fruto de um estágio realizado na Universidade do Minho em Portugal, intitulado “Application of cork from stoppers as adsorbent for water and wastewater treatment using Ciprofloxacin as pharmaceutical model”.

1.1. OBJETIVO GERAL

Estudar o tratamento de lixiviado de aterro sanitário (LAS) através da aplicação do processo FEF de forma unitária e/ou integrada com oxidação biológica, investigando os subprodutos gerados e a diminuição dos níveis de toxicidade de amostras tratadas.

1.2. OBJETIVOS ESPECÍFICOS

- Caracterizar e avaliar as composições químicas e físicas do LAS;
- Realizar testes preliminares no reator de foto-eletro degradação aplicado no tratamento do LAS;
- Definir as condições operacionais otimizadas a partir de uma metodologia de superfície de resposta;
- Realizar corridas experimentais com eletrodos de ferro;
- Identificar a formação de possíveis subprodutos durante as reações de FEF unitária e processo FEF combinado com oxidação biológica;
- Estudar a melhor estratégia de integração de sistemas (FEF+Bio ou Bio+FEF);
- Realizar testes de toxicidade com bioindicadores áquaticos;

[redacted]2. REVISÃO DA LITERATURA

2.1. PRODUÇÃO DE RESÍDUOS SÓLIDOS NO BRASIL E SUA DISPOSIÇÃO EM ATERROS SANITÁRIOS

Segundo a 19ª edição do Panorama dos Resíduos Sólidos no Brasil, publicado pela Associação Brasileira de Empresas de Limpeza Pública e Resíduos Especiais (ABRELPE), a geração total de resíduos sólidos urbanos (RSU) no Brasil em 2020 foi de 82,5 milhões de toneladas de RSU (ABRELPE - ASSOCIAÇÃO BRASILEIRA DE EMPRESAS DE LIMPEZA PÚBLICA E RESÍDUOS ESPECIAIS, 2020). Estes resíduos devem sofrer destinação correta, e segundo a Legislação Brasileira vigente, Lei Federal n. 12.305/2010, que institui a Política Nacional de Resíduos Sólidos (BRASIL, 2010), os aterros sanitários emergem como uma técnica de destinação final ambientalmente adequada. Sendo estas técnicas de tratamento de resíduos empregadas em diversos municípios brasileiros.

Os aterros sanitários são obras de engenharia, destinados à disposição de rejeitos que visam à proteção da saúde pública e do meio ambiente. Estes apresentam uma forma viável de disposição final de resíduos sólidos urbanos podendo propiciar a recuperação de áreas abandonadas, principalmente pelo fato de que em seus projetos são contemplados sistemas que evitam impactos ambientais (EL-SALAM; ABU-ZUID, 2015; MCBEAN; ROVERS; FARQUHAR; 1995).

Contudo, outros impactos surgem da geração de gases e efluentes líquidos, se estes não forem bem controlados. Estes impactos incluem explosões, danos à fauna e flora, odores desagradáveis, lixiviação de efluentes ocasionando a contaminação de aquíferos e poluição do ar (YOUCAI; ZIYANG, 2017).

Como subproduto da degradação da matéria orgânica aterrada, bem como da umidade dos resíduos aterrados, é produzido o chorume, o qual é percolado pelas águas pluviais, originando assim o LAS, que é considerado o principal problema ambiental de aterros sanitários, já que este apresenta composição heterogênea e geração contínua (CHEMLAL et al., 2014; GUPTA et al., 2014; KJELDSEN et al., 2002; RENOU et al., 2008).

As características do LAS variam em função das condições socioeconômicas, geográficas e climáticas de determinado local, sendo que os tipos de resíduos aterrados e técnicas empregadas para a compactação são fatores determinantes nas cinéticas de degradação biológicas que ocorrem no aterro. Os micro-organismos precursores da degradação da matéria orgânica em aterros sanitários são em sua maioria anaeróbios, sendo o processo de biodegradação dividido em diferentes fases (KJELDSEN et al., 2002; MCBEAN; ROVERS; FARQUHAR; 1995; RENOU et al., 2008).

2.2. FASES DE DECOMPOSIÇÃO DA MATÉRIA ORGÂNICA EM ATERROS SANITÁRIOS

As características e a composição dos resíduos sólidos são de grande importância para determinar o grau e a taxa em que os mesmos se decompõem, assim como os subprodutos que serão produzidos. Esta decomposição de caráter biológico ocorre em três fases distintas, cada qual com suas próprias características (MCBEAN; ROVERS; FARQUHAR; 1995).

Para melhor entendimento das condições de determinado LAS, é pertinente estudar as fases pelas quais ele é gerado nos aterros, sendo estas descritas por: El-Salam; Abu-Zuid, (2015); Kjeldsen et al., (2002); McBean; Rovers; Farquhar; (1995); Renou et al., (2008):

1) Fase de decomposição aeróbia: ocorre nas fases iniciais quando ainda há presença de oxigênio. Nesta fase os micro-organismos aeróbios degradam a matéria orgânica a dióxido de carbono (CO_2), água e resíduos orgânicos parcialmente degradados, produzindo calor. A elevada quantidade de CO_2 produzida nesta fase forma ácido carbônico o que resulta em um LAS com pH ácido.
2) Decomposição anaeróbia (fase anaeróbia): envolve micro-organismos facultativos, que se tornam dominantes quando esgota-se o oxigênio. Nesta fase também chamada de acetogênese são produzidas elevadas concentrações de ácidos orgânicos, amônia, hidrogênio e dióxido de carbono. A produção de CO_2 e grandes quantidades de ácidos orgânicos resultam na queda do pH (5,5-6,5)

o que causa a dissolução de outros compostos orgânicos e inorgânicos, tornando o LAS agressivo e com elevada condutividade.

3) Decomposição anaeróbia (metanogênese): as bactérias metanogênicas trabalham lentamente para degradar o substrato, produzindo dióxido de carbono, metano e água. Estas utilizam os produtos da decomposição anaeróbia como hidrogênio e ácido acético, assim há uma elevação no pH (7,0-8,0), tornando o LAS menos agressivo. Os ácidos orgânicos que não são assimilados pelas bactérias são convertidos em metano por um processo intermediário. Ácidos graxos atuam como substrato, porém elevadas concentrações destes são tóxicos para as bactérias metanogênicas.

2.3. CARACTERÍSTICAS DE LAS

Em um estudo recente Naveen et al. (2017) realizou a caracterização físico-química e biológica detalhada de lixiviados de aterros sanitários, citando-se como principais características e a razão de sua presença, os seguintes itens:

- O pH é dependente da degradação de compostos orgânicos no aterro, sendo produzido dióxido de carbono e pequena quantidade de amônia, que posteriormente resulta na formação de íons de amônia e ácido carbônico. O ácido carbônico é dissociado com facilidade para produção de cátions hidrogênio e ânions bicarbonato, que influenciam os níveis de pH do sistema. Além disto, materiais e gases dissolvidos modificam o pH do meio, sendo a alcalinidade causada pela presença de bicarbonatos, carbonatos e íons hidroxil. Em LAS valores de alcalinidade costumam ser elevados, devido à decomposição bioquímica e processo de dissolução que ocorre nos aterros (NAVEEN et al., 2017).

- Condutividade e sólidos totais dissolvidos são influenciados pela quantidade total de materiais orgânicos e inorgânicos presentes em solução, e são utilizados para representar o grau de salinidade e constituintes minerais do LAS. O conteúdo salino dos LAS é devido à presença de potássio, sódio, cloreto, nitrato, sulfato, amônia, etc, já os elevados valores de condutividade são atribuídos a elevados níveis de cátions e ânions. Elevada presença de sólidos totais dissolvidos podem reduzir a penetração de luz, o que diminui a fotossíntese e aumenta a temperatura da água, prejudicando o crescimento e desenvolvimento de bactérias fotossintéticas e algas (SCANDELAI et al., 2018).

- A presença de ânions no LAS geralmente está relacionada ao alto conteúdo de cloretos. Além disto, a presença de outros ânions pode ser consequência da qualidade de resíduos aterrados: sulfatos, são resultado da disposição de resíduos de construção ou cinzas, detergentes e resíduos inertes, como sedimentos de rios dragados, nos aterros; nitratos são primeiramente formados como resultado da oxidação de amônio para nitrito e subsequente para nitratos pelo processo de nitrificação; nitratos e fosfatos resultam da decomposição e mineralização da matéria orgânica e são importantes nutrientes para o crescimento de plantas, então no meio aquático são os principais responsáveis por eutrofização (NAVEEN et al., 2017).
- Cátions em LAS tipicamente são associados à presença de cálcio, magnésio, sódio e potássio. A presença destes está relacionada à composição da massa de resíduos aterrados e a fase predominante de estabilização do aterro, sendo que a presença de potássio em água subterrânea é frequentemente utilizada como indicador de poluição por LAS (CHRISTENSEN et al., 2001).
- A presença de metais confere toxicidade ao LAS e impacta de forma negativa o crescimento da microflora que auxilia na degradação do LAS. Os principais metais encontrados em LAS são o ferro, zinco e níquel, e em menores concentrações tem-se o cromo, cobre, cádmio e chumbo. A presença de metais é considerada perigosa, principalmente devido a possibilidade de contaminação de solos, os tornando improdutíveis (NAVEEN et al., 2017).
- A relação existente entre a idade do aterro sanitário e a composição da matéria orgânica, pode propiciar um critério útil para escolha de um processo de tratamento adequado, sendo a idade do aterro sanitário um fator de grande relevância a ser considerado quando se trata da qualidade do LAS (MCBEAN; ROVERS; FARQUHAR; 1995).

Assim, denomina-se lixiviado jovem o chorume produzido nos primeiros 4 anos de operação do aterro sanitário, nestes a atividade biológica está mais ativa e corresponde a fase ácida da degradação anaeróbia, no entanto, segundo estudos, estes são os mais poluídos em comparação com aterros mais antigos. pHs em torno de 6,0 indicam fase jovem de degradação do LAS (EL-SALAM; ABU-ZUID, 2015; GUPTA et al., 2014; KJELDSEN et al., 2002; MCBEAN; ROVERS; FARQUHAR; 1995; YOUCAI; ZIYANG, 2017).

A fração DBO_5/DQO pode ser utilizada para estimar as condições de biodegradabilidade do LAS visto que ela corresponde à quantidade de matéria orgânica que pode ser oxidada biologicamente pela quantidade de matéria orgânica que pode ser oxidada quimicamente. Assim, frações DBO_5/DQO iguais ou maiores a 0,6 representam boas condições de biodegradabilidade do LAS, por outro lado, frações DBO_5/DQO menores que 0,3 classificam o LAS como recalcitrante (BAIJU et al., 2018; COMNINELLIS et al., 2008).

Após 4-5 anos, o lixiviado denominado maduro sofre um aumento no pH para cerca de 7-8 (JORSTAD; JANKOWSKI; ACWORTH, 2004). LAS maduros, apresentam uma fração DBO_5/DQO menor ($DBO_5/DQO<0,3$) (BAIJU et al., 2018), apresentando pouca biodegradabilidade, sendo então considerados LAS estabilizados. As mudanças ocorrem como resultado da oxidação dos compostos orgânicos biodegradáveis, tais como os ácidos orgânicos, e da produção de gases (MCBEAN; ROVERS; FARQUHAR; 1995). Os compostos orgânicos de difícil biodegradação permanecem, relacionados principalmente a presença de ácidos húmicos e fúlvicos (JURCZYK; KOC-JURCZYK, 2017; SILVA et al., 2016). Nesta fase há um aumento na concentração de bactérias metanogênicas, que por sua vez produzem um líquido com características básicas. Além disto, estes micro-organismos convertem os ácidos orgânicos voláteis para biogás (CH_4 e CO_2), contendo espécies muito mais recalcitrantes do que as produzidas nas fases preliminares de decomposição, além de elevadas concentrações de amônia (GUPTA et al., 2014; JURCZYK; KOC-JURCZYK, 2017; KJELDSEN et al., 2002, 2002; MCBEAN; ROVERS; FARQUHAR; 1995; RENOU et al., 2008).

Características como baixos valores da fração DBO_5/DQO e elevadas concentrações de compostos orgânicos refratários, com elevado peso molecular inviabilizam o tratamento do LAS por processos biológicos, sendo que compostos como hidrocarbonetos, halogênio e bifenilas policloradas podem criar um efeito inibitório e reduzir a eficiência de sistemas biológicos (BAIJU et al., 2018; WISZNIOWSKI et al., 2006). Sendo assim, técnicas de tratamento físico-químicas são indicadas como as mais adequadas para o tratamento de LAS maduros (BAIJU et al., 2018).

Além disto, a presença de contaminantes emergentes em LAS e seus efeitos de sinergia entre outros contaminantes e no meio ambiente, vem aumentando a preocupação quanto a técnicas de tratamento capazes de remover estes compostos, visto que tratamentos convencionais geralmente não removem estas moléculas complexas (BERGMAN; UNITED NATIONS ENVIRONMENT PROGRAMME; WORLD HEALTH ORGANIZATION, 2013; PETRIE; BARDEN; KASPRZYK-HORDERN, 2015; TOURAUD et al., 2011; WEE; ARIS, 2017). Dentre os contaminantes que vem sendo identificados em LAS, que o atribui elevados níveis de toxicidade, pode-se citar os químicos desreguladores endócrinos (EDCs) (BADERNA et al., 2011; DARBRE, 2015; HE et al., 2009; HOU et al., 2017; KLAUCK et al., 2017a; QI et al., 2018; REIS et al., 2017).

Um estudo mais detalhado abordando a presença de EDCs, seu tratamento e degradação por procesos baseados em reações Fenton encontra-se descrito no capítulo 3.

2.4. TRATAMENTOS APLICADOS A LAS

O LAS apresenta condições tóxicas, portanto deve ser tratado antes da descarga no ambiente receptor (GONG et al., 2016b). Os sistemas mais usuais empregados para o tratamento de LAS são baseados em processos físico-químicos e/ou biológicos. Alguns dos tratamentos físico-químicos mais aplicados são os biorreatores com membranas (SUI et al., 2017), separação por membranas (CHAUDHARI; MURTHY, 2010), coagulação seguida da floculação e decantação (LONG et al., 2017) e tratamentos de oxidação biológica (ROBINSON, 2017).

Processos de separação por membranas como o de microfiltração que objetiva a remoção de partículas coloidais e suspensas são indicados como etapa de polimento ou pré-tratamento a outro processo com membranas (ultrafiltração, nano-filtração ou osmose reversa), sendo seu emprego isoladamente omitido para o tratamento de LAS. Piatkiewicz et al. (2001) estudaram esta técnica como etapa de pré-filtração para o tratamento de um

LAS, onde não encontraram significativas taxas de retenção de DQO, limitando a eficiência de remoção em cerca de 25-35%.

A ultrafiltração é considerada eficiente para eliminar macromoléculas e particulados, mas as taxas de retenção são fortemente dependentes do material pelo qual a membrana é confeccionada, apresentando remoção entre 10 a 75% (PENG, 2017).

Linde; Jönsson, (1995) estudaram o comportamento de membranas aplicadas a nanofiltração de LAS, e reportaram que a maior parte dos metais que são cátions multivalentes são repelidos enquanto que cátions monovalentes que são substancias mais perigosas passam pela membrana, sendo a retenção de cadmio, zinco, chumbo e cromo em cerca de 70% enquanto que a retenção de potássio e sódio foi menor que 10%. Investigações realizadas por Vogel; Bilitewski; Nghiem, (2007) concluíram que o entupimento das membranas (*fouling*) é devido a combinação de cálcio e matéria orgânica. Portanto, o entupimento das membranas se torna um inconveniente relacionado a estes processos, sendo que resulta em diminuição das taxas de eficiência, visto que os LAS apresentam elevadas concentrações de sais e partículas coloidais orgânicas.

Processos de osmose reserva também vêm sendo estudados para o tratamento de LAS. Li; Wichmann; Heine, (2009) investigaram um sistema de filtração de LAS em módulo espiral. O estudo mostrou resultados satisfatórios para filtração direta do LAS pelo sistema de modulo em espiral. Contudo um concentrado era produzido, e uma grande atenção devia ser destinada para limpeza química das membranas, evitando *fouling*, sendo este um fator determinante no desempenho destes sistemas.

Dentre os processos físico-químicos o processo de coagulação e floculação é comumente empregado, sendo o cloreto férrico descrito como coagulante mais eficiente para a remoção de matéria orgânica do LAS (BAKRAOUY et al., 2017; NTAMPOU; ZOUBOULIS; SAMARAS, 2006; ZHOU et al., 2011).

Long et al. (2017) estudaram o processo de coagulação para o tratamento de um LAS concentrado e reportaram que a coagulação foi essencial para remoção de matéria orgânica suspensa, sólidos e cor, obtendo a maior remoção de COT (78%) em pH da solução 4,0 e empregando cloreto férrico ($FeCL_3$) como coagulante, no entanto não foi alcançada uma concentração ótima de coagulante, pois as taxas de remoção de COT aumentaram conforme a concentração de coagulante aumentou.

Bakraouy et al. (2017) também identificaram este fenômeno, sendo a remoção de COD linearmente relacionada com a concentração de coagulante ($FeCL_3$) e floculante. No entanto, a uma determinada concentração de reagentes adicionados, a eficiência não foi melhorada, o que foi relacionado à quebra de flocos devido ao excesso de reagentes adicionados. Estes autores reportaram que mesmo que uma dose de coagulante otimizada seja obtida (adição de cátions), os coloides tornam-se positivamente carregados, devido a absorção de cátions em sua superfície, e como resultado disto, os coloides recuperam seu estado estável sob ação de forças de repulsão elétrica (LI et al., 2010b). Baseados nisso, as eficiências de remoção limitaram-se a 20-96%.

Processos de oxidação biológica geralmente são aplicados para o tratamento de águas residuárias devido a sua simplicidade de instalação e operação. A biodegradação da matéria orgânica é realizada pelos micro-organismos que podem degradar compostos orgânicos a dióxido de carbono (CO_2) e lodo sob condições aeróbicas e biogás sob condições anaeróbicas (RENOU et al., 2008).

Processos biológicos tem se mostrado eficientes para remoção de matéria orgânica e nitrogenada de LAS jovens ($DBO_5/COD>0,5$). Contudo, conforme o LAS se torna maduro, as condições de recalcitrância se elevam devido à presença de ácidos húmicos e fúlvicos, o que limita a eficiência do processo (KARGI; PAMUKOGLU, 2003; VILAR et al., 2011).

Yahmed et al. (2009) investigaram a eficiência de um processo de oxidação biológica baseado em reatores de biofilme imersos e fixos em condições aeróbicas para o tratamento de LAS que apresentou condições de biodegradabilidade ($DBO_5/COD=0,4$). Resultados obtidos demonstraram taxas de redução de COT entre 60 e 90%. Em outro estudo em que investigaram-se a degradação biológica através de digestão anóxica (condição de baixa oxigenação) para o tratamento de um LAS realizado por Trabelsi et al. (2009), foi reportado que após um tempo de retenção de 90 dias, foi possível reduzir 91% de DBO_5; 46% DQO; 65% COT e 45% de anomia.

Dessa forma, os principais desafios das tecnologias de tratamento de água e efluentes são a remoção de poluentes refratários aos métodos de tratamento convencionais (CANLE; FERNÁNDEZ PÉREZ; SANTABALLA, 2017) e sua mineralização ou transformação completa em espécies orgânicas inofensivas (PAHIGIAN; ZUO, 2018).

Como uma tecnologia de tratamento promissora, os processos avançados de oxidação (POAs) e os processos eletroquímicos avançados de oxidação (EPOAs) têm se apresentado como soluções viáveis para o tratamento de LAS, uma vez que poderiam alcançar a remoção e mineralização da matéria orgânica refratária (Fernandes et al., 2015a; Mandal et al., 2017), íons inorgânicos (DENG et al., 2018) e EDCs (SEIBERT et al., 2019a; WANG; SUN; BIAN, 2010) devido à sua oxidação não seletiva realizada por •OH.

2.5. Processos de Oxidação Avançada (POA)

Dentre as técnicas emergentes de tratamento de efluentes, os POA têm se destacado entre a comunidade científica apresentando potencial de aplicabilidade industrial. Estes proporcionam elevados índices de eficiência sendo capazes de oxidar compostos orgânicos recalcitrantes, e não apenas os transferir de fase (MALATO et al., 2002).

Os POA consistem basicamente na combinação de uma série de reações químicas envolvendo a oxirredução (pela adição de um oxidante) de íons catalíticos e/ou semicondutores com o objetivo principal de gerar *in situ* um poderoso agente oxidante, o radical hidroxila ($^{\bullet}$OH). Quando submetidos à irradiação UV, a excitação molecular dos compostos metálicos proporciona uma maior velocidade em seus ciclos de oxirredução e regeneração, aumentando significativamente a eficiência e a velocidade da reação (BRILLAS; SIRÉS; OTURAN, 2009; MALATO et al., 2009; MOREIRA et al., 2017; VENU et al., 2014).

Malato et al. (2009) relatam que a versatilidade dos POA é aprimorada pelo fato de que existem diferentes formas de produzir os $^{\bullet}$OH, conforme o requisito de cada tratamento. Métodos baseados em UV-vis (fotólise), H_2O_2/UV, O_3/UV e H_2O_2/O_3/UV usam a fotocatálise do H_2O_2 e O_3 para produzir os radicais. Já outros métodos como a fotocatálise heterogênea e homogênea, são baseados no uso de uma vasta gama de semicondutores (Fe, TiO_2, ZnO entre outros) e adição de H_2O_2 e irradiação com luz UV-vis. A diferença entre sistemas homogêneos e heterogêneos se dá pela presença de catalisadores semicondutores em fase sólida, nos sistemas heterogêneos (TEIXEIRA; JARDIM; 2004).

Dentre os POAs comumente estudados, destaca-se os processos Fenton e foto-Fenton.

2.5.1. Processo Fenton (PF)

O processo Fenton envolve a adição de reagentes (H_2O_2 e Fe^{2+}). A reação Fenton foi observada pela primeira vez por Fenton, (1894) e é baseada na transferência de elétrons entre H_2O_2 e um íon metálico, neste caso íons ferrosos (Fe^{2+}) atuam como catalisador (Equação 1). As reações do tipo Fenton possuem grande potencial de gerar espécies oxidantes para a degradação de poluentes (PIGNATELLO; OLIVEROS; MACKAY, 2006). A mistura de H_2O_2 e Fe^{2+} produz radicais hidroxila que possuem elevado potencial de oxidação da matéria orgânica presente em efluentes (FENTON, 1894), sendo que a degradação dos compostos orgânicos depende da sua interação com os $^{\bullet}OH$. Além disto, os reagentes empregados são de fácil obtenção, relativamente baratos e seguros (PIGNATELLO; OLIVEROS; MACKAY, 2006).

$$Fe(II)_{(aq)} + H_2O_2 \rightarrow Fe(III)_{(aq)} + OH^{\bullet} + OH^{-} \qquad (1)$$

Os $^{\bullet}OH$ atacam os poluentes orgânicos, podendo levar a sua completa transformação em CO_2, água e íons inorgânicos como produto final da reação, ou seja, provocando sua mineralização (DENG; ENGLEHARDT, 2006; PIGNATELLO; OLIVEROS; MACKAY, 2006).

A geração dos radicais hidroxila no processo Fenton é rápida, e pode ser definida como a dissociação de H_2O_2 na presença de ferro como catalisador. No entanto, a reação é completada em meio reacional ácido, ou seja, na presença de íons H^+, possibilitando a decomposição de H_2O_2 (Equação 2), enquanto que o ferro desempenha o papel de catalisador da reação, alternando-se pelas formas de Fe^{2+} e Fe^{3+} (UMAR; AZIZ; YUSOFF, 2010).

Sendo assim, pH ácidos são reportados como os mais adequados para que a reação Fenton ocorra (DENG; ENGLEHARDT, 2006; GUPTA et al., 2014; VILAR et al., 2011).

$$2Fe(II) + H_2O_2 + 2H^+ \rightarrow 2Fe(III) + 2H_2O \qquad (2)$$

Jung et al. (2017a) estudaram a oxidação química de um LAS através do processo Fenton, realizando variações no pH da solução e na razão H_2O_2/Fe^{2+}. Como resultado puderam concluir que um elevado pH inibe a decomposição de H_2O_2 para formação de $^{\bullet}OH$, realçando o auto-decaimento de H_2O_2, desativando o catalisador de Fe^{2+} através da formação de hidróxidos sólidos de ferro, favorecendo a presença de carbonatos e bicarbonatos, que sequestram $^{\bullet}OH$, e reduzem o potencial dos $^{\bullet}OH$, ao passo que pH mais baixos retardam a reação entre Fe^{2+} e Fe^{3+} com H_2O_2 e aumentam o efeito de H^+ nos $^{\bullet}OH$. Quanto à razão H_2O_2/Fe^{2+}, os autores acima citados identificaram que H_2O_2 é mais importante para reação, porque sua concentração limita a produção teórica de $^{\bullet}OH$, enquanto que o ferro serve apenas como catalisador, concluindo que elevadas H_2O_2/Fe^{2+} favorecem o efeito de consumo de $^{\bullet}OH$ pelo H_2O_2, provocando menores taxas de remoção.

2.5.2. Processo foto-Fenton (PFF)

O processo foto-Fenton apresenta duas principais características: a redução de Fe^{3+} a Fe^{2+} para produzir mais radicais hidroxila via fotólise e a foto-descarboxilização de compostos férricos (DENG; ENGLEHARDT, 2006; KAVITHA; PALANIVELU, 2004; KIM; VOGELPOHL, 1998).

Os íons ferrosos foto-gerados participam da reação Fenton, gerando $^{\bullet}OH$ adicionais, com isto aceleram o processo de oxidação, comparado com o Fenton (KAVITHA; PALANIVELU, 2004). Uma vez que na presença de luz os ácidos orgânicos de baixa massa molecular (oxálico, acético e fórmico) são degradados via reação fotocatalítica com Fe(III), já no processo Fenton não alcançam total degradação (PIGNATELLO; OLIVEROS; MACKAY, 2006).

A foto-redução do Fe^{3+} a Fe^{2+} é considerada como responsável pelo aumento do efeito oxidativo do processo. O Fe^{2+} reage com o peróxido de hidrogênio (H_2O_2) dando sequência a reação de Fenton (Equação 1). Na Equação 3 ocorre a reação de fotorredução do Fe^{3+} para o Fe^{2+}, que apresenta velocidade de reação maior do que na reação Fenton. O Fe^{3+} pode interagir com o excesso de H_2O_2 ou $^{\bullet}HO_2$ restaurando o Fe^{2+} na reação (Equação 4). O Fe^{2+} reage com o H_2O_2 em meio ácido gerando Fe^{3+} e água. Ainda, a fotólise de H_2O_2 gera dois radicais hidroxila (Equação 5), podendo ocorrer simultaneamente ao processo foto-Fenton. Compostos de ferro absorvem energia em um comprimento de onda acima de 400 nm, permitindo o uso de energia solar, enquanto promovem a foto-redução (Equação 6) (BAUTISTA et al., 2008; DENG; ENGLEHARDT, 2006; NOGUEIRA et al., 2007; PIGNATELLO; OLIVEROS; MACKAY, 2006).

$$Fe(III)_{(aq)} + H_2O_2 \rightarrow Fe(II)_{(aq)} + {}^{\bullet}HO_2 + H^{+}{}_{\text{(aq)}} \tag{3}$$

$$Fe(III)_{(aq)} + {}^{\bullet}HO_2 \rightarrow Fe(II)_{(aq)} + O_2H^{+} \tag{4}$$

$$H_2O_2 + hv \rightarrow 2\ OH^{\bullet} \tag{5}$$

$$FeOH^{2+} + hv \rightarrow Fe(II) + OH^{\bullet} \tag{6}$$

O PFF mostra-se ser o mais apto de todos os POAs para ser conduzido com luz solar, porque a solubilidade de hidróxidos de ferro e especialmente complexos de ácidos ferro-orgânicos absorvem parte do espectro de luz visível, não somente radiação ultravioleta. Como consequência há uma eficiente produção de radicais disponíveis para o processo de oxidação. A exposição de fótons pode ser realizada a luz solar este é o fator mais importante do ponto de vista econômico, podendo ser crucial para reduzir custos (MALATO et al., 2009).

Estudos realizados utilizando PFF para a remoção de contaminantes orgânicos costumam apresentar uma taxa de degradação ou uma taxa de conversão de poluentes como função de dois parâmetros equivalentes: a quantidade total de energia solar UVA recebida por unidade de volume de água tratada, Q_{UVA}, (kJ L^{-1}); ou o tempo de exposição normalizada calculada pelas condições padrões de irradiância UVA W m^{-2}, em determinado tempo de exposição (min.). Esses parâmetros são confiáveis para a avaliação da degradação da matéria orgânica na água para diferentes reatores solares, uma vez que a taxa de remoção de poluentes é proporcional à quantidade de fótons que entram no sistema, necessários para foto ativar o processo de foto-Fenton (MALATO et al., 2009). Sarria et al. (2003) reportaram que o PFF vem sendo aplicado para a remoção da toxicidade de efluentes de difícil tratamento, e que a perda de toxicidade após o tratamento vem acompanhada de uma melhora na biodegradabilidade das amostras tratadas.

Outro fator que possui influência no processo é a presença de fosfatos, devido a sua precipitação com íons férricos, além de outros íons como halogênios e sulfatos que formam complexos com o catalisador alterando sua atividade e/ou promovendo a formação de radicais menos reativos que os radicais hidroxila. A formação destes complexos é largamente dependente do pH e da concentração destes em solução, visto que a precipitação de íons de ferro é favorecida em pH elevados (neutro a básico) (DE LAAT; TRUONG LE; LEGUBE, 2004).

Uma das alternativas para evitar a necessidade de acidificação da solução para manter ferro solúvel e estável na solução é mediar a reação foto-Fenton na presença de agentes complexantes (SUN; PIGNATELLO, 1992). Estes complexos são foto-ativados na região espectral do visível, podendo beneficiar a cinética da reação (NOGUEIRA; OLIVEIRA; PATERLINI, 2005). Sendo assim, a necessidade de um meio reacional ácido para manter os íons catalíticos solúveis é reportada como o principal inconveniente do PFF. Seibert et al. (2017) investigaram a degradação de um LAS mediante a aplicação do PFF induzido com complexantes orgânicos e reportaram que com o uso de agentes quelantes possibilitou-se elevadas remoções de cor, compostos aromáticos, nitrogênio, carbono orgânico dissolvido, DBO_5, DQO, melhorando as condições de biodegradabilidade (DBO_5/DQO) das amostras tratadas em pH próximos da neutralidade.

2.6. Processos Eletro-Oxidativos Avançados

Para o melhor entendimento dos processos e reatores eletroquímicos, é conveniente retomar algumas noções básicas, de acordo com Lefrou; Fabry; Poignet, (2012).

Corrente pode ser designada como o movimento de espécies carregadas que correspondem a um fluxo de cargas. À medida que espécies carregadas possuem massa, a noção de corrente é relacionada ao transporte de massa. Já a densidade de corrente (j) que é um vetor com módulo expresso em (A m^{-1}), representa o fluxo de cargas de um modo geral (LEFROU; FABRY; POIGNET, 2012).

Eletrodo é o objeto que pode variar de acordo com a situação. Por definição: quando ocorre uma simples reação redox, o eletrodo onde ocorre a oxidação é chamado de ânodo, e o eletrodo onde ocorre a redução é chamado de cátodo (LEFROU; FABRY; POIGNET, 2012).

A voltagem de uma célula eletroquímica é denotada por U, e corresponde à diferença de potencial entre os dois terminais da célula, expresso em V (volts). Já a polaridade de um eletrodo é definida de acordo com o símbolo da voltagem da célula. Por exemplo, se a célula é positiva, a polaridade (+) é atribuída ao eletrodo de trabalho, podendo ser chamado de eletrodo positivo ou ânodo. A polaridade (–) é atribuída ao eletrodo oposto, que também pode ser chamada de eletrodo negativo ou cátodo (LEFROU; FABRY; POIGNET, 2012).

Não há uma conexão entre a polaridade do eletrodo e o papel que desempenham (ânodo ou cátodo). Então dependendo das condições do sistema um eletrodo pode ser um ânodo ou cátodo, e também mudar sua polaridade, por convenção (LEFROU; FABRY; POIGNET, 2012):

A densidade é positiva se o eletrodo esta em um campo de oxidação $I>0$. A densidade é negativa se o eletrodo esta em um campo de redução $I<0$.

Os reatores de PEOAs podem apresentar configurações variadas, sendo a intensidade de corrente, pH, temperatura, agitação, área e material dos ânodos e cátodos e quando aplicado, quantidade de H_2O_2 e de íons férricos adicionados os principais parâmetros estudados, cujos resultados são encontrados em diversas pesquisas (MOREIRA et al., 2015; MÜLLER et al., 2015; PANIZZA; CERISOLA, 2009; VENU et al., 2014).

2.6.1. Oxidação Anódica (OA)

O mais simples e popular método de EPOAs empregado é a oxidação anódica (OA). Nesta a oxidação dos poluentes acontece por transferência de elétrons da superfície do eletrodo, produção de espécies reativas de oxigênio como intermediários da oxidação da água a oxigênio, incluindo o poderoso $^{\bullet}OH$ adsorvido, na superfície do ânodo, denominado $M(^{\bullet}OH)$ (Equação 7), e produção de oxidantes mais fracos, como H_2O_2 (Equação 8) através da dimerização de $M(^{\bullet}OH)$ e formação de O_3 pela descarga de água no ânodo (Equação 9) além de formação de outros oxidantes fracos que são produzidos eletroquimicamente a partir dos íons existentes na solução (COMNINELLIS, 1994; PANIZZA; CERISOLA, 2009).

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (7)$$

$$2M(^{\bullet}OH) \rightarrow 2MO + H_2O_2 \quad (8)$$

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^- \quad (9)$$

Pesquisas tem demonstrado que a eficiência do processo está relacionada com a capacidade de troca de massa entre a solução e os ânodos e também relacionada ao material pelo qual os eletrodos são confeccionados (MOREIRA et al., 2017; PANIZZA; CERISOLA, 2009). Panizza e Cerisola, (2009) trazem como regra: quanto maior o potencial para desenvolvimento de O_2 do material do ânodo, mais fraca é a interação entre $M(^{\bullet}OH)$ com a superfície do ânodo, e mais elevada será a reatividade química para oxidação dos compostos orgânicos. Ainda segundo estes autores, o processo pode ser melhorado pela ação de oxidantes que podem ser eletricamente gerados a partir de agentes existentes na solução como cloro, sulfato, fosfato, carbonato e oxigênio. Enquanto que cloro gasoso, persulfato, perfosfato e percarbonato são produzidos a partir da oxidação anódica, o H_2O_2 é gerado a partir da redução catódica (MOREIRA et al., 2017).

O H_2O_2 pode ser gerado na massa a partir de duas eletrorreduções do oxigênio (diretamente injetado como gás ou ar dissolvido) na superfície do cátodo em meio ácido/neutro (Equação 10). Contudo em soluções alcalinas o oxigênio é reduzido a íon hidroperoxido (HO_2^-) a base conjugada do H_2O_2 que apresenta menor poder de oxidação (E. BRILLAS et al., 1997; FOLLER; BOMBARD, 1995).

$$O_{2(g)} + 2H^+ + e^- \rightarrow H_2O_2 \tag{10}$$

Reações parasitárias como redução eletroquímica de H_2O_2 na superfície do cátodo (Equação 11) e em menor grau, dissolução de H_2O_2 na massa (Equação 12) podem ocorrer usando células únicas e divididas (GALLEGOS; GARCÍA; ZAMUDIO, 2005). O H_2O_2 também pode ser oxidado a oxigênio no ânodo, produzindo o oxidante mais fraco, hidroperoxil ($HO_2^{\bullet}$) como intermediário (Equações 13 e 14) (BRILLAS et al., 1995). Para atingir a máxima eletrogeração de H_2O_2, o contato entre cátodo, oxigênio e água deve ser maximizado, por esta razão são preferíveis cátodos porosos (MOREIRA et al., 2017).

$$H_2O_2 \rightarrow OH_2^{\bullet} + H^+ + e^- \tag{11}$$

$$OH_2^{\bullet} \rightarrow O_2 + H^+ + e^- \tag{12}$$

$$H_2O_2 \rightarrow OH_2^{\bullet} + H^+ + e^- \tag{13}$$

$$OH_2^{\bullet} \rightarrow O_2 + H^+ + e^- \tag{14}$$

Processos eletroquímicos com H_2O_2 são geralmente realizados na presença de Fe^{2+} para a produção de reagente Fenton, porque apenas o H_2O_2 em si é um oxidante moderado a forte (CAMPOS-MARTIN; BLANCO-BRIEVA; FIERRO, 2006; MOREIRA et al., 2017).

2.6.2. Eletro-Fenton (EF)

Dependendo das configurações e do material dos eletrodos, nos processos PEOAs os poluentes podem ser removidos por eletro-oxidação direta – elétrons são transferidos diretamente do ânodo – ou eletro-oxidação indireta – envolve a geração de espécies eletro-ativas (MANDAL; DUBEY; GUPTA, 2017).

Processos EF e FEF fazem uso da eletro-oxidação indireta, como resultado da reação de desenvolvimento do oxigênio durante a descarga de água, assim o oxigênio dissolvido é transferido para a superfície do cátodo, adsorvido no cátodo e reduzido eletroquimicamente para produzir peróxido de hidrogênio em meios ácidos, espécies oxidantes são formadas e adsorvidas na superfície do ânodo, atuando como precursores da oxidação (MANDAL; DUBEY; GUPTA, 2017; PANIZZA; CERISOLA, 2009; WANG et al., 2010).

A clássica reação Fenton é uma mistura de H_2O_2 e Fe^{2+}, levando a produção de $^{\bullet}OH$ (Equação 1), um poderoso agente oxidante (FENTON, 1894). Já a reação de eletro-Fenton compreende i) a eletrogeração de H_2O_2 contínua e *in situ* em cátodos alimentados com oxigênio ou ar (Equação 10); ii) adição de Fe^{2+} à solução, como catalisador e iii) redução catódica de Fe^{3+} para Fe^{2+} com consequente continua produção de reagente Fenton (Equação 15) (BRILLAS; SIRÉS; OTURAN, 2009).

No processo EF a oxidação dos orgânicos ocorre via uma oxidação eletroquímica indireta através de radicais hidroxila, gerados pela reação Fenton. Neste processo ambas espécies H_2O_2 (Equação 10) e Fe^{2+} (Equação 16) podem ser eletro-geradas *in situ* a partir dos eletrodos (DENG; ENGLEHARDT, 2006).

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad (15)$$

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (16)$$

Para esse processo células divididas ou não divididas podem ser empregadas. Quando uma célula não dividida é usada, o EF conta ainda com a produção de espécies reativas de oxigênio (ROS) no ânodo, principalmente $M(^{\bullet}OH)$ (MOREIRA et al., 2017). Além disto, os reatores podem apresentar diferentes configurações: íons ferrosos adicionados externamente e ambos H_2O_2 e Fe^{2+} gerados no cátodo; fornecimento externo de H_2O_2, sendo um ânodo de ferro de sacrifício usado como fonte de ferro; adição externa de H_2O_2 e ferro eletrogerado via redução de íons férrico ou lodo de hidróxido férrico; ou eletrogeração de Fe^{2+} e H_2O_2 (via duas eletro-reduções de oxigêno aspergido) no ânodo de sacrifício e no cátodo respectivamente (ORKUN; KULEYIN, 2012).

Durante o processo EF, radicais hidroxila podem ser produzidos na superfície de um ânodo de elevado sobrepotencial de oxigênio a partir da oxidação da água (ZHANG; ZHANG; ZHOU, 2006). A produção de radicais ainda pode ser aumentada com a contínua regeneração de Fe^{2+} no cátodo, reduzindo a produção de lodo férrico (SIRÉS et al., 2007; ZHANG et al., 2012).

H_2O_2 é a principal fonte de radicais hidroxila no processo EF e baixas concentrações de H_2O_2 não irão gerar radicais suficientes para proporcionar relativos decréscimos da matéria orgânica. Contudo a efetividade decresce quando a dosagem é aumentada até uma determinada concentração. Neste caso pode ocorrer um efeito de “sequestro” de radicais hidroxila que pode resultar em flotação do lodo férrico ou decréscimo da sedimentação do lodo, por causa do O_2 fora de gaseificação, recombinação de radicais hidroxila, e/ou a formação de pequenas cadeias de ácidos orgânicos de difícil oxidação, reduzindo a eficiência de remoção (NIDHEESH; GANDHIMATHI, 2012; UMAR; AZIZ; YUSOFF, 2010; ZHANG et al., 2014).

Quando elevadas concentrações de íons catalíticos de ferro são adicionadas também pode haver uma redução nas taxas de remoção de poluentes, sendo este comportamento associado ao consumo de radicais hidroxila causados pelo excesso de íons ferrosos através de uma reação competitiva entre radicais hidroxila e íons ferrosos, os quais podem diminuir a concentração dos radicais (NIDHEESH; GANDHIMATHI, 2012; ZHANG et al., 2014).

Conforme reportado por Wang et al. (2012) o decréscimo da eficiência de redução dos componentes orgânicos deve-se principalmente à precipitação de espécies $Fe(OH)_3$ no cátodo devido a elevadas doses de $FeSO_4$, as quais diminuíram os sítios ativos no cátodo para produção de H_2O_2. Os autores afirmam que existe uma fração ótima de $[H_2O_2]/[Fe^{2+}]$ para a remoção dos compostos orgânicos. Baixas frações $[H_2O_2]/[Fe^{2+}]$ podem levar a um rápido desaparecimento de radicais hidroxila e íons ferrosos. Por outro lado, elevadas frações $[H_2O_2]/[Fe^{2+}]$ podem melhorar a reação entre H_2O_2 e radicais hidroxila, e levar a produção de radical hidroperoxila, uma espécie com poder de oxidação menor quando comparado com radicais hidroxila. Portanto quando esta $[H_2O_2]/[Fe^{2+}]$ for ótima, o consumo de radicais hidroxila por Fe^{2+} ou H_2O_2 será mínimo (ZHANG; ZHANG; ZHOU, 2006). Sendo assim, estudos anteriores tem reportado que a fração $[H_2O_2]/[Fe^{2+}]$ ótima para o LAS varia entre 1 a 12 (MOHAJERI et al., 2010; WANG et al., 2012; ZHANG et al., 2014; ZHANG; ZHANG; ZHOU, 2006).

No entanto juntamente com o processo de eletro-Fenton, dependendo do pH do meio, o processo de eletrocoagulação também pode ocorrer simultaneamente, através do mecanismos no qual Fe^{2+} e Fe^{3+} são convertidos em espécies $Fe(OH)_n$ e os poluentes podem ser removidos pela atração eletrostática e/ou reações de complexação (ATMACA, 2009).

2.6.3. Foto-eletro Fenton (FEF)

O processo FEF faz uso da reação Fenton, com a assistência de radiação. No processo EF, ocorre a regeneração eletroquímica de Fe^{2+} a partir de espécies Fe^{3+} e a formação de peróxido de hidrogênio por uma redução de 2 elétrons de O_2 dissolvido na superfície do cátodo, o que leva a geração de $^{\bullet}OH$ a partir da decomposição do H_2O_2 (MONTEIL et al., 2018; RADHA; SIRISHA, 2018).

Para a formação de H_2O_2, um pH ácido é requerido. Contudo, em valores de pH muito baixo (pH=2,0), ocorre a formação de peroxônio (H_2O^{3+}), o que não é interessante porque peroxônio não reage muito bem com Fe^{2+}, assim a formação de $^{\bullet}OH$ não é muito eficiente. Por outro lado, valores elevados de pH da solução implicam na decomposição do H_2O_2 em água e oxigênio (FENG et al., 2003; WANG et al., 2010; WANG; LEMLEY, 2001). PH também tem relação com as espécies de ferro em solução. Em pH muito ácido (pH<1) complexos entre H_2O_2 e Fe^{2+} são formados, o que reduz a eficiência do processo, bem como em valores de pH da solução maiores que 4,0 (pH>4), espécies de Fe^{3+} precipitam na forma de $Fe(OH)_3$ (PIGNATELLO, 1992).

Com o auxílio da radiação, mais $^{\bullet}OH$ são produzidos devido à excitação e recuperação de Fe^{2+} (BRILLAS; SIRÉS; OTURAN, 2009; SIRÉS; BRILLAS, 2012) e intermediários da oxidação ou complexos de Fe(III) são fotolisados, o que também permite a regeneração de Fe^{2+} (RADHA; SIRISHA, 2018).

Nos tratamentos foto-assistidos a degradação dos poluentes é acelerada principalmente por: i) foto-redução de complexos de Fe(III)-hidroxil, como os mais foto-ativos $FeOH^{2+}$ em pH próximo de 3 (Equação 17) (SUN; PIGNATELLO, 1993), com consequente produção de •OH e regeneração de Fe^{2+}, e ii) a fotólise direta por excitação de transferência de carga do ligante para metal de complexos formados entre Fe^{3+} e alguns orgânicos, denominados ácidos carboxílicos (Equação 18) (FAUST; ZEPP, 1993; MOREIRA et al., 2017; ZUO; HOIGNE, 1992), permitindo a regeneração de Fe^{2+} em paralelo com a formação de espécies oxidantes mais fracas tais como radical ânion superóxido, radical ânion dióxido carbono e H_2O_2 (MOREIRA et al., 2017).

$$FeOH^{2+} + hv \rightarrow Fe^{2+} + OH^{\bullet} \tag{17}$$
$$Fe^{3+}(L)_n + hv \rightarrow Fe^{2+}(L)_{n-1} + L_{ox}^{\bullet} \tag{18}$$

Dependendo do comprimento de onda e intensidade de radiação, os poluentes podem ser degradados por diferentes mecanismos e com aumento da taxa de degradação para maiores intensidades de radiação, sendo que a radiação pode ser fornecida por lâmpadas de diferentes comprimentos de onda UVA (λ=315-400 nm), UVB (λ=280-315 nm) e UVC (λ<280 nm) (MOREIRA et al., 2017). A foto-redução de complexos foto-ativos Fe(III)-hidróxidos (Equação 17) e a fotólise de complexos de Fe^{3+} com orgânicos (Equação 18) ocorrem sob radiação UV-Vis e a fotólise direta dos poluentes pode ocorrer quando a fonte de luz emite radiação no mesmo comprimento de onda que os contaminantes podem absorver eficientemente. A aplicação de luz UVC na presença de peróxidos simétricos tais como H_2O_2 podem levar a geração adicional de $^{\bullet}OH$ através da clivagem homolítica da ligação do peróxido (-O-O-), (Equação 19) (BAXENDALE; WILSON, 1957; GLAZE; KANG; CHAPIN, 1987; VENKATADRI; PETERS, 1993) o que não ocorre em outros comprimentos de onda (MOREIRA et al., 2017). A radiação UVC também acelera a fotorredução de espécies de ferro foto-ativas (Equação 20) (BRILLAS; SIRÉS; OTURAN, 2009).

$$H_2O_2 + hv \rightarrow 2\,OH^{\bullet} \tag{19}$$
$$[Fe(OH)]^{2+} + hv \rightarrow Fe^{2+} + OH^{\bullet} \tag{20}$$

Quando utilizado a luz solar como fonte de energia é comum obter maiores taxas de degradação devido a elevada intensidade UV da luz solar com emissão na região do visível (λ>400 nm) assim também levando a formação de complexos Fe(III)-carboxilicos com a fotólise direta (Equação 18) (MOREIRA et al., 2017).

Quanto à intensidade de corrente aplicada, um aumento na corrente aplicada previsivelmente irá levar a um aumento da eletrogeração de Fe^{2+} de Fe^{3+} (Equação 15), o que por sua vez irá aumentar a eficiência da cadeia de reação Fenton (ZHANG; ZHANG; ZHOU, 2006). Contudo sob aplicação de elevadas densidades de corrente, reações de competição podem acontecer entre os eletrodos, tais como descarga de oxigênio no ânodo (Equação 21) e desenvolvimento de hidrogênio no cátodo (Equação 22) aumentando e inibindo as reações de produção de radicais hidroxila na superfície do ânodo devido a oxidação da água (Equação 7) e produção de radicais hidroxila pela regeneração de Fe^{2+} na superfície do cátodo (Equação 15) (FERNANDES et al., 2015; ZHANG; ZHANG; ZHOU, 2006). Além disto, elevadas correntes representam aumento de custo com energia elétrica (ATMACA, 2009). Assim a quantidade de corrente aplicada aos eletrodos precisar ser determinada cuidadosamente para evitar consumo de energia adicional (FERNANDES et al., 2015).

$$2H_2O_2 \rightarrow 4H^+ + 2O_{2(g)} + 4e^- \qquad (21)$$

$$2H^+ + 2e^- \rightarrow \ H_{2(g)} \qquad (22)$$

Autores apontam que 50 Am^{-2} é a mínima densidade de corrente requerida para alcançar uma eficiência na oxidação dos orgânicos presentes no LAS, caso contrário o LAS pode se tornar escuro e marrom, precipitações podem ser formadas na superfície do ânodo em condições de oxidativas fracas, sendo que geralmente, um aumento na densidade de corrente aumenta a remoção de DQO e nitrogênio amoniacal (COSSU et al., 1998; FERNANDES et al., 2015).

A distância entre eletrodos também afeta a remoção de poluentes. Se os eletrodos estão localizados muito próximos, o Fe^{2+} eletro-regenerado pode ser facilmente oxidado a íons férricos no ânodo, o que poderia inibir a reação Fenton (ZHANG; ZHANG; ZHOU, 2006). Por outro lado, a diminuição na distância entre os eletrodos poderia levar a uma diminuição do potencial de fluxo de elétrons através do eletrólito e um decréscimo equivalente da voltagem da célula e de consumo de energia (FERNANDES et al., 2015). Grandes distâncias entre os eletrodos limitam a transferência de massa de íons férricos da superfície do cátodo que governa a regeneração de íons ferrosos, sendo que distâncias de 1,3 a 2,1 cm proporcionaram remoções de DQO semelhantes (ZHANG; ZHANG; ZHOU, 2006). De acordo com Atmaca, (2009), aumentar a distância entre os eletrodos significantemente aumentará o custo com energia do processo EF, sendo assim a mínima distância seria a mais indicada (FERNANDES et al., 2015).

De acordo com Anglada; Urtiaga; Ortiz, (2009); Deng; Englehardt, (2006); Fernandes et al. (2015); e Martínez-Huitle; Ferro, (2006) a oxidação eletroquímica de um efluente, pode apresentar os seguintes mecanismos de oxidação: i) conversão eletroquímica, na qual compostos orgânicos são parcialmente oxidados e transformados em subprodutos mais biodegradáveis, sendo ainda um pós tratamento requerido, geralmente empregado um processo de tratamento biológico; ii) combustão eletroquímica, onde os compostos orgânicos são completamente mineralizados e transformados em água, dióxido de carbono e espécies inorgânicos, não sendo necessários tratamentos posteriores.

Sendo assim, PEOAs são uma alternativa de tratamento promissora, principalmente para remoção e mineralização de contaminantes presentes em efluentes e soluções complexas, apresentando ainda, a versatilidade de serem combinados com outras técnicas de tratamento.

[redacted]3. ARTIGO 1: PRESENCE OF ENDOCRINE DISRUPTING CHEMICALS IN SANITARY LANDFILL LEACHATE, ITS TREATMENT AND DEGRADATION BY FENTON BASED PROCESSES: A REVIEW

Em consonância com as normas do Programa de Pós-graduação em Engenharia Química (Resolução nº 057/2020/CTC, Art. 59º), o primeiro artigo foi redigido de acordo com as regras da revista Process Safety and Environmental Protection.

Presence of endocrine disrupting chemicals in sanitary landfill leachate, its treatment and degradation by Fenton based processes: A review

Daiana Seibert[1,♣], Heloise Quesada[1], Rosângela Bergamasco[1], Fernando Henrique Borba[2], Leandro Pellenz[2]

[1] *Postgraduate Program of Chemical Engineering, State University of Maringa, UEM, Av. Colombo, 5790, Maringa, Parana, CEP: 87020-900, Brazil*

[2] *Postgraduate Program of Environment and Sustainable Technologies, Federal University of Fronteira Sul, UFFS, Rua Jacob Reinaldo Haupenthal 1580, 97900-00, Cerro Largo, RS, Brazil.*

♣ Corresponding author

Tel.: +55 (55) 99606 9881, E-mail: daiaseibert@hotmail.com (Daiana Seibert)

Permanent address: Universidade Federal da Fronteira Sul-UFFS, Rua Jacob Reinaldo Haupenthal, 1580, Sala 104, Bloco dos Professores. Bairro Industrial, 97900-00, Cerro Largo, RS, Brazil.

Highlights

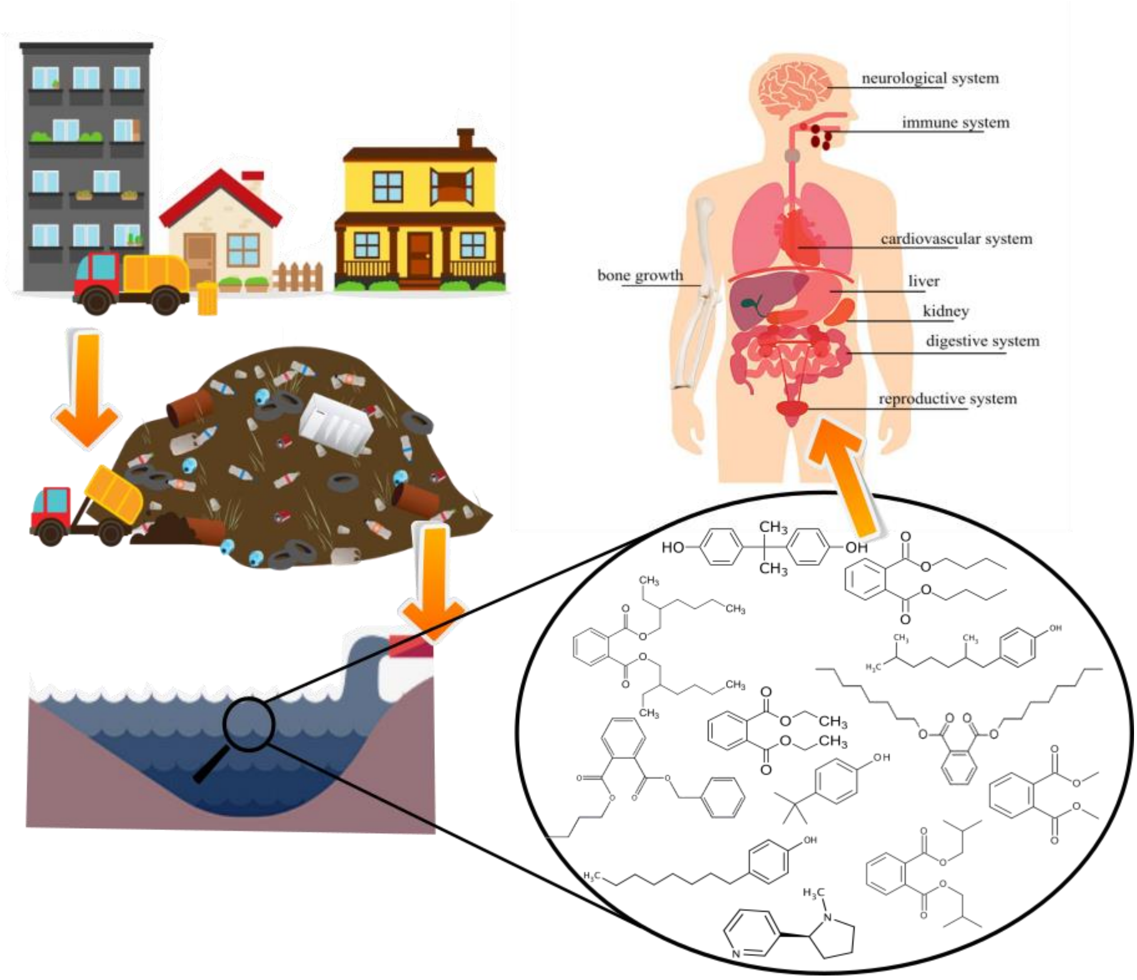
EDCs from a variety of classes have been detected in landfills over 13 countries;
Need for effective control regulation on segregation and recycling of solid waste;
BPA, PAEs and surfactants are the most frequent EDCs detected in SLL;
$^{\bullet}$OH produced by Fenton-based processes are able to mineralize EDCs;
Degradation pathway of EDCs in a SLL matrix should be investigated.

Abstract

Various studies concerning sanitary landfill leachate (SLL) characteristics and toxicity identified the presence of endocrine disrupting chemicals (EDCs). A review of the detected EDCs in SLL was performed, in which the 12 most frequent EDCs identified in sanitary landfill sites over the world were ranked: BPA, DBP, DEHP, DEP, NP, BBP, DOP, DMP, 4OP, DiBP, DTBP and nicotine. The presence of these compounds is related to the activities on the dumping site, especially by the presence of plastic and personal care products, insecticides and cleaning agents in the waste bulk. Many diseases in human and animals have been associated with exposure to EDCs, as examples can be cited: disorder in metabolic processes that might end in diaseases, reduction of fertility, bioaccumulation and a high cancer potential. Among the treatment strategies applied to SLL degradation, processes based on Fenton reaction have received increasing attention due to its non-selective oxidation performed by hydroxyl radicals ($^{\bullet}$OH). Thus, they are able to oxidize/mineralize compounds which are not removed in conventional wastewater treatments. Degradation pathways and byproducts produced after the oxidative process may provide important information around the applicability of these techniques. Integrated treatments are also studied to obtain biosafety of treated wastewater samples. For the SLL treatment, the most employed strategy coupled to Fenton-based processes is the biological oxidation. The integration strategy relies on the SLL characteristics, being two modalities allowed: Fenton-based processes followed by biological systems or the opposite one. Future researches are needed to advance our understanding of the behavior of EDCs in human and animals bodies, as well as its critic concentrations. Also, there still is a lack of research regarding the degradation pathway of EDCs by •OH in a SLL matrix, the ecofriendly disposal of iron sludge, the handle of the chemical solution wastes and the economic aspects of these treatments in order to meet a large scale application of this technology. Therefore, these topics have been discussed in this review article.

Keywords: Emerging contaminants; Endocrine disruptoring chemicals; Advanced oxidation process; Sanitary landfill leachate treatment.

Graphical abstract



3.1. INTRODUCTION

Landfills sites are considered the most widely practiced methods for the disposal of products at the end of their useful life (Baderna et al., 2011; Clarke et al., 2015), especially because in the last decades the population growth and rapid urbanization increased the per capita waste generation (Baderna et al., 2019; Renou et al., 2008).

In the landfill site, the municipal solid waste (MSW) undergoes through decomposition by physical, chemical and microbial processes which transfer pollutants from the MSW to the percolating water originating the sanitary landfill leachate (SLL) (Baderna et al., 2011; Vahčič et al., 2011). However, the composition of the MSW present in landfills, landfill age, geological and weather conditions coupled with the quantity of leachate generated will determine the type and concentration of chemicals present in SLL (Clarke et al., 2015; Khalil et al., 2018).

The produced SLL poses challenges for landfill operators worldwide, if SLL treatment plants were not adequately built and maintained, it represents a potential contaminant to soils, surface water, aquifers and sea water due to leaching of different pollutants, which may be harmful to organisms, including human and environmental receptors (Baderna et al., 2011; Khalil et al., 2018; Vahčič et al., 2011). As a consequence, compounds present in SLL can be accumulated in the successive links of the food chain or in long-term exposure by human beings (Sang and Li, 2004; Widziewicz et al., 2012).

SLL is considered a wastewater of severe hazard for human because it is generally toxic, mutagenic, genotoxic and estrogenic, even at low concentrations (Baderna et al., 2019). Among the toxic compounds detected in SLL, currently, more attention is giving for the presence of endocrine disruptor chemicals (EDCs). The main concern about the presence of these compounds in SLL is due to its persistence to conventional wastewater treatment plants (WWTP), which directly affects the public health, since EDCs are the source of several anomalies that affect human and animals, such as genotoxicity, potential cancer compounds, anxiety, depression, and hyperactivity (Bergman et al., 2013; Canle et al., 2017; Colborn et al., 1993; Endocrine Society, 2019; Monneret, 2017).

According to EPA, (1997) an EDC can be defined as “an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior”. In this regard, important considerations for assessing adverse effects of EDCs are dose, body burden, timing, and duration of exposure at critical periods of life (EPA, 1997).

EDCs from a variety of classes have been identified in SLL: bisphenol A (BPA) (Asakura et al., 2004; Fudala-Ksiazek et al., 2018a; Wang et al., 2016), phthalic acid esters (PAEs) (Fudala-Ksiazek et al., 2018a; Gong et al., 2016a; Hong et al., 2017), pharmaceutical (Clarke et al., 2015; Yi et al., 2017), hormones (Behnisch et al., 2001; Kapelewska et al., 2016; Pesci Pereira et al., 2018), phenol (Boonnorat et al., 2016; Ramírez-Sosa et al., 2013), alkanes (Khalil et al., 2018; Klauck et al., 2017), nicotine (Baderna et al., 2011; Khalil et al., 2018; Reis et al., 2017), polycyclic aromatic hydrocarbon (He et al., 2015; Li et al., 2016a; Turki et al., 2013), parabens (Kapelewska et al., 2016), halogen (Li et al., 2016a), organotin compounds (Vahčič et al., 2011) and carboxylic acid (Reis et al., 2017).

Recent studies detected high amounts of BPA and several PAEs in treated and untreated SLL samples (Fudala-Ksiazek et al., 2018a; Hong et al., 2017; Seibert et al., 2019), thus the presence of these EDCs has received increasing attention because of their potential adverse health effects on animals and humans and about efficient treatment process capable to complete remove them (Fudala-Ksiazek et al., 2018a-b).

The cytotoxicity of SLL was studied by Khalil et al. (2018) that identified short-term damaged in blood and organs such as the liver coupled with significant damages at the DNA levels in exposed animals through *in vivo* tests. Therefore, the exposure of humans to water contaminated by SLL presents high risks of developing adverse health effects (Baderna et al., 2011). Furthermore, the interaction between chemicals present in SLL makes it virtually impossible to establish the true toxicity and genotoxicity of SLL by detecting individual chemicals (Khalil et al., 2018). Faced with this, SLL should undergo by WWTP before its discharge on the environment.

The most common treatment applied to SLL is biological systems. Their use is widespread mainly because of its reliability, simplicity and high cost-effectiveness (Renou et al., 2008). Nonetheless, mature SLL usually presents high levels of recalcitrant organic compounds related to the presence of humic and fulvic acids, therefore the application of biological oxidation present limited efficiency (Kargi and Pamukoglu, 2003; Vilar et al., 2011; Widziewicz et al., 2012). Besides that, temperature control, high retention time, large territorial use, difficulty in reach discharge standards and variability of seasonal conditions can be cited as challenges for the biological treatment of SLL in WWTP (Peng, 2017). For these reasons, advanced processes that are able to completely remove/degrade pollutants present in SLL, or to degrade the remaining compounds in biologically treated SLL, have been increasingly investigated by researchers (Baiju et al., 2018; Gao et al., 2015; Kurniawan et al., 2006; Pesci Pereira et al., 2018; Renou et al., 2008).

Among the emerging techniques applied for wastewater treatment, Fenton-based processes have received increasing attention, since they are able to oxidize recalcitrant organic compounds and not only transfer their phase (Zazouli et al., 2012). These processes are based on the combination of a series of chemical reactions aiming the *in situ* production of powerful oxidizing species, such hydroxyl radicals (•OH). The classic Fenton reaction, which involves hydrogen peroxide and a ferrous ion, can be assisted by UV irradiation (photo-Fenton) or electric current (electro-Fenton), significantly increasing its efficiency (Brillas et al., 2009; Malato et al., 2002, 2009; Moreira et al., 2017; Venu et al., 2014). For these reasons Pesci Pereira et al. (2018) reported that a tertiary treatment such AOPs is necessary to degrade the remaining compounds in an SLL biological treatment. For example, Wang et al. (2016) reduced the genotoxic effects and the levels of nonylphenol (NP) and BPA from an SLL to under the detection limit with UV-Fenton suggesting the higher removal efficiency of the AOP process.

In this way, the aim of this review study was to identify the EDCs present in SLL over the world, classify the main frequent EDCs detected and its risks to human and animals, as well as investigate the treatment strategies applied to the SLL degradation, highlighting the application of Fenton reaction and its derivation and the mechanisms behind the SLL degradation by Fenton based processes.

3.2. EDCS AND ITS PRESENCE IN SLL

High concentrations of persistent organic pollutants have been detected in the aquatic environment, increasing its toxicity levels (Radha and Sirisha, 2018). Examples of these pollutants are pharmaceutical, pesticides, personal care products, and EDCs, which even at trace levels, may cause adverse effects in water supplies (Barışçı et al., 2018; Benitez et al., 2011; Tamura et al., 2017; Yi et al., 2017). The main source of EDCs discharge in the environment originates from the consumption of manufactured products such as: fragrances, flame retardants, paints, surfactants, plastics, adhesives, lubricants, seals, detergents, disinfectants, cleaning products, building materials, household appliances, furniture, textile products (Benson, 2009; Lorber and Koch, 2013; Wee and Aris, 2017).

It has been reported that EDCs may enter into the environment by different pathways including WWTP, septic systems and soil contamination (Canle et al., 2017; Quesada et al., 2019; Yi et al., 2017). As reported by Liu et al. (2013), PAEs were detected in high concentrations in drinking water sources in China, because of its persistence/low removal by the WWTP. However, SLL may represent a significant source of EDCs in the environment (Clarke et al., 2015; Yi et al., 2017). Furthermore, substances released as components of complex mixtures in SLL can produce additive, synergistic or antagonistic interactions (Fernández and Beiras, 2001; Simmons and Berman, 1989). Among target EDCs detected in SLL, concentrations of BPA (1800 times), dibutyl phthalate (DBP) (10 times), butyl benzyl phthalate (BBP) (40 times), and di(2-ethylhexyl) phthalate (DEHP) (30 times) in leachate were more than ten times higher than those detected in surface water (Asakura and Matsuto, 2009). Although the detection of trace compounds in SLL is still a difficult task (Kapelewska et al., 2016) nowadays many persistent compounds have been identified in this wastewater (Behnisch et al., 2001; Pesci Pereira et al., 2018; Reis et al., 2017). The presence of persistent pollutants and EDCs in SLL might be connected to the disposal activities in the dumping site (Coors et al., 2003; Yi et al., 2017) especially because throughout the landfill stabilization process, organic materials are released by the degradation of the waste, which gives rise to a high level of organic matter in the SLL (Fang et al., 2009).

A review on EDCs identified in sanitary landfill sites over the world was performed and the results are presented in Table 1. These compounds were identified as EDCs based on the US. Environmental Protection Agency–USEPA, (2012) list.

Table 1. EDCs detected in sanitary landfills over the world, as well as its toxicity levels and applied treatment if performed.

EDCs detected in raw SLL	Country	Toxicity level	Identification method	Ref.
N,N-diethyl-3-methylbenzamide, triallyl isocyanurate, O-toluene ethyl sulfonamide, cyclohexane,1,1,3-trimethyl-2-(3methylpentyl), 1-3-cyclohexanedione,2,4,6-trimethyl, DiBP, dipentyl phthalate, BPA	Brazil	Toxic to *Artemia salina*	GC-MS	(Seibert et al., 2019)
Oleamide, (hentriacontane and eicosane), Hexanedioic acid, bis(2-ethylhexyl), Tributylamine, DEHP, nicotine	Lebanon	Acute toxicity to mice. Significant DNA damages in tested organisms	GC-MS	(Khalil et al., 2018)
17b-estradiol, estriol, and 17aethynylestradiol	Brazil	np	HPLC and estrogenic activity	(Pesci Pereira et al., 2018)
DMP, DEP, BPA	Poland	np	GC-MS	(Fudala-Ksiazek et al., 2018a)
acetaminophen, BPA, clofibric acid, caffeine, N,N-diethyl-m-toluamide (DEET), gemfibrozil, lincomycin, salicylic acid, and sulfamethazine	Singapore	np	UHPLC-MS/MS and isotope dilution	(Yi et al., 2017)
DMP, DBP, DEHP	China	Acute toxic effect to *D. Magna* with genotoxic and cytotoxic potency.	GC-MS	(Hong et al., 2017)

Decane, Dodecane, Eicosane, Nonadecane, Nonane, Octadecane, Tetradecane, Undecane	Brazil	High toxicity to *Allium cepa*	GC-MS	(Klauck et al., 2017)
3-methylbenzoic acid, Cyclohexanone, Styrene, N,N-diethylformamide, N, N-dimethylacetamide, Benzaldehyde, Isocyanatocyclohexane, N-butylbenzenesulfonamide, N-ethyl-4-methylbenzenesulfonamide, Triethyl phosphate, nicotine, 2-methylphenol, menthol, propanoic acid, 4-tert-butylbenzoic acid, Hexanal, dioctyl hexanedioate, N,N-diethyl-3-methylbenzamide, N,N-dimethylformamide, BPA, 4-tert-butylphenol, 2-phenylpropan-2-ol, Tetradecane	Brazil	Toxic to Aliivibrio fischeri	GC-MS	(Reis et al., 2017)
BPA, 2,6-di-tert-butylphenol, dichlorophenol, DEP, DBP	Thailand	np	GC-MS	(Boonnorat et al., 2016)
methylparaben, ethylparaben, propylparaben, buthylparaben, benzophenone (BPh), 3-(4-methylbenzylidene)camphor, DEET, estrone, β-estradiol	Poland	np	GC-MS	(Kapelewska et al., 2016)
DEP, DOP, benzyl butyl phthalate,	China	np	GC-MS	(Li et al., 2016b)

acenaphthene, fluorine, naphthalene, fluoranthene,				
NP, BPA	China	Genotoxic and cytotoxic potency	HPLC–MS	(G. Wang et al., 2016a)
BPA, 4OP, DBP, DOP, DEHP	China	Caused disturbances in the endocrine and reproduction systems.	GC–MS, UPLC-MS/MS, and GC-ECD	(Gong et al., 2016a)
Carbamazepine, gemfibrozil, primidone, sulfamethoxazole, trimethoprim, Perfluorooctanoic acid	USA	np	UHPLC-MS/MS	(Clarke et al., 2015)
Toluene, ethylbenzene, chlorobenzene, DMP, DEP, DBP, DOP	China	Biotoxicity to luminescent bacteria	GC	(He et al., 2015)
Aniline, 4-Methyl-phenol, 2,4-Bis(1,1-dimethylethyl)-phenol, 3,5-Di-tert-butyl-4-hydroxyphenyl propionic acid, 4,40-(1-Methylethylidene)bis-phenol, Mono (2-ethylhexyl) ester 1,2-benzenedicarboxylic acid	Mexico	Identified EDCs have toxic properties	GC-MS	(Ramírez-Sosa et al., 2013)
BPA, anthracene, DBP, 1-2 benzenedicarboxylic acid, Bis (2-methoxyethyl) ester, Mono (2-ethylhexyl) ester 1,2-benzenedicarboxylic acid	Tunisia	Inhibited tomato germination so has toxic effect	GC-MS	(Turki et al., 2013)

Dichloromethane, Benzene,	Poland	Acute toxic to the fauna and microflora	GC-MS	(Kwasniewska et al., 2012)
BPA, 2,2,6,6-tetramethyl-4-piperidinol, nicotine	Italy	Inhibited cell growth Toxic to aquatic and mammal species.	GC-MS	(Baderna et al., 2011)
monomethyltin, dimethyltin, monobutyltin, dibutyltin, tributyltin, monooctyltin, dioctyltin	Slovenia	np	GC–ICP-MS	(Vahčič et al., 2011)
BPA, NP, 4OP	Japan	Toxic and estrogenic potential to fish	GC–MS and LC–MS	(Kamata et al., 2011)
BPA,4-t-butylphenol, N-ethyltoluenesulfoneamide (NETSA)	Japan	Toxic to V. fischeri	CG-MS	(Lei and Aoyama, 2010)
BPA, DBP, BBP, DEHP	Japan	np	CG-MS	(Asakura and Matsuto, 2009)
BPA, DEP, DiBP	China	np	GC-FID/HPLC	(He et al., 2009)
DEHP, DiBP	China	np	GC-FID	(Zheng et al., 2009)
DMP, DBP, DOP	China	np	HPLC	(Fang et al., 2009)
cyclohexanecarboxylic acid	China	np	GC-MS	(Lei et al., 2007)
DiBP, DEHP	China	np	GC-FID	(Zheng et al., 2007)
4OP, NP, BPA, DEP, DBP, BBP, DEHP, Tributylin, Triphenyltin	Japan	np	GG-MS	(Asakura et al., 2004)
BPA, NP	Germany	Estrogenic activity	GC-MS	(Coors et al., 2003)
BPA	Japan	np	GC-MS	(Yamamoto et al., 2001)

BPA, NP, DBP, BBP, 17aethynylestradiol, 4OP	Japan	Estrogenic activity	GG-MS	(Behnisch et al., 2001)

[*] np: not performed.

Abbreviations: bisphenol A (BPA); Dibutyl phthalate (DBP); Di(2-ethylhexyl) phthalate (DEHP); Diethyl phthalate (DEP); Nonylphenol (NP); Butyl benzyl phthalate (BBP); Dioctyl phthalate (DOP); Dimethyl phthalate (DMP); 4-Octylphenol (4OP); 4-tert-butylphenol (DTBP); Diisobutyl phthalate (DiBP); gas chromatography (GC); gas chromatography-mass spectrometry (CG-MS); high performance liquid chromatography (HPLC); liquid chromatography- mass spectrometry (UHPLC-MS/MS); gas chromatography-electron capture detection (GC-ECD); liquid chromatography–mass spectrometry (LC–MS); GC-FID/HPLC; gas chromatography-flame ionization detector (GC-FID).

Samples from many countries of different continents were studied and present something in commom, the presence of EDCs. Analyzing Table 1 it is possible to observe that many EDCs from different classes were detected in SLL. Besides that, according to the toxicity tests performed, it is possible to identify that all of them present aggregate toxicity, highlighting the toxic effects to aquatic organisms and significant DNA damage, which confirms the potential human health and the environment risk.

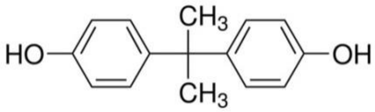
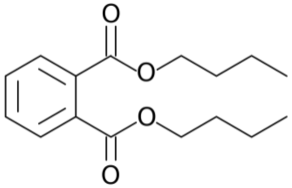
Turki et al. (2013) reported that phenolic compounds, aromatic acids, aliphatic acid and ester, polycyclic aromatic hydrocarbons (PAHs), PAES and alcohols were detected in the raw and most of the treated leachates. Among these, 4-methyl-phenol and 2,4-bis-phenol present toxic properties.

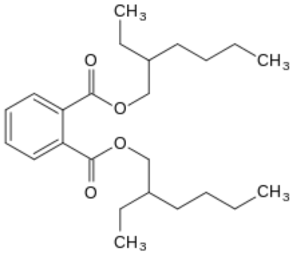
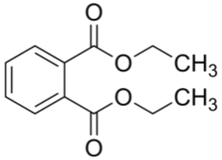
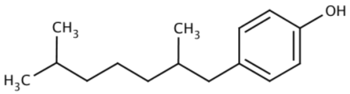
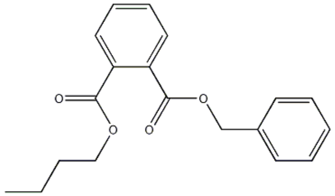
Nonionic surface activates, paint, and plastics should be the main contributors to the inflow of alkylphenols, BPA and PAEs into landfill sites (Asakura et al., 2004). PAEs are only physically rather than chemically bonded to the plastic structure, thus they may be easily released from the plastic products and leach into the environment where they tend to be stable because of its low water solubility and high octanol-water partition coefficients (Asakura et al., 2004; Fang et al., 2009).

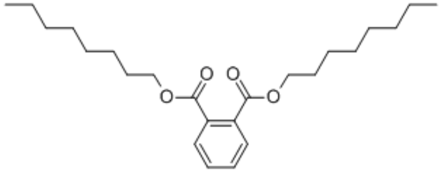
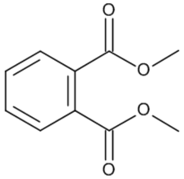
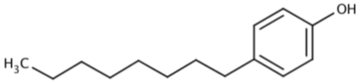
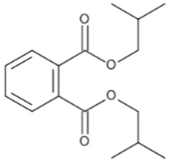
Among the EDCs identified in SLL, BPA and PAEs represent important pollutants, so investigation into these compounds have been increasing (Fudala-Ksiazek et al., 2018a; Lei and Aoyama, 2010; Qi et al., 2018; Reis et al., 2017; Sharma et al., 2019, 2015). Especially because these compounds are considered responsible for the estrogenicity of the wastewater (Baderna et al., 2019).

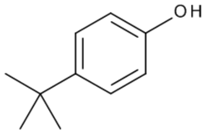
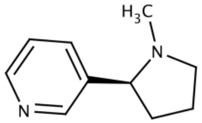
EDCs identified in Table 1 were ranked into the most frequent detected compounds. Thus, Table 2 presents the 12 EDCs commonly identified in sanitary landfills over the world, its use and detected concentrations.

Table 2. Frequent EDCs identified in dumping sites over the world as well as the EDCs common uses and detected concentration.

EDC	**CAS number**	**Use**	**Conc. (μg L^{-1})**	**Ref.**
Bisphenol A (BPA) 	80-05-7	Production of polycarbonates and epoxy resins used in various industries	0.13-17200	(Yi et al., 2017) (Coors et al., 2003) (Baderna et al., 2011) (Asakura et al., 2004) (Asakura and Matsuto, 2009) (Turki et al., 2013) (Behnisch et al., 2001) (Reis et al., 2017) (Boonnorat et al., 2016) (Fudala-Ksiazek et al., 2018a) (Lei and Aoyama, 2010) (He et al., 2009) (Yamamoto et al., 2001) (Kamata et al., 2011) (Wang et al., 2016a) (Gong et al., 2016a) (Seibert et al., 2019)
Dibutyl phthalate (DBP) 	84-74-2	PVC plastics and nitrocellulose lacquers (varnish)	1-1700	(Hong et al., 2017) (Asakura et al., 2004) (Asakura and Matsuto, 2009) (Turki et al., 2013) (Fang et al., 2009) (Behnisch et al., 2001) (Boonnorat et al., 2016) (He et al., 2015) (Gong et al., 2016a)
Di(2-ethylhexyl) phthalate (DEHP)	117-81-7	Plastic industry including medical ware	18.16-298	(Khalil et al., 2018) (Hong et al., 2017) (Asakura et al., 2004) (Asakura and Matsuto, 2009) (He et al., 2009) (Zheng et al., 2009) (Zheng et al., 2007) (Gong et al., 2016a)

				
Diethyl phthalate (DEP) 	84-66-2	Plastic industry, insecticides, drugs, cosmetics	1-1370	(Asakura et al., 2004) (Li et al., 2016b) (Boonnorat et al., 2016) (Fudala-Ksiazek et al., 2018a) (He et al., 2015)
Nonylphenol (NP) 	25154-52-3	Surfactants	0.07-5.5	(Coors et al., 2003) (Asakura et al., 2004) (Behnisch et al., 2001) (Kamata et al., 2011) (G. Wang et al., 2016a)
Butyl benzyl phthalate (BBP) 	85-68-7	Plastic industry	7.8	(Asakura et al., 2004) (Asakura and Matsuto, 2009) (Li et al., 2016b) (Behnisch et al., 2001)
Dioctyl phthalate (DOP)	117-84-	Plastics,	90-460	(Li et al., 2016b) (Fang et al., 2009) (He et al., 2015) (Gong et al.,

	0	pesticides and cosmetics		2016a)
Dimethyl phthalate (DMP) 	131-11-3	Plastic industry	1-1710	(Hong et al., 2017) (Fang et al., 2009) (Fudala-Ksiazek et al., 2018a) (He et al., 2015)
4-Octylphenol (4OP) 	1806-26-4	Surfactants used in detergents, pesticide formulations, plastics and emulsifiers	0.31-4.37	(Asakura et al., 2004) (Behnisch et al., 2001) (Kamata et al., 2011) (Gong et al., 2016a)
Diisobutyl phthalate (DiBP) 	84-69-5	Plastic industry	1	(He et al., 2009) (Zheng et al., 2009) (Zheng et al., 2007) (Seibert et al., 2019)
4-tert-butylphenol (DTBP)	98-54-4	Raw material for polymerization,	-	(Reis et al., 2017) (Boonnorat et al., 2016) (Lei and Aoyama, 2010)

		inhibitor and stabilizing agent in the chemical industry		
Nicotine 	54-11-5	Insecticide, tobacco	0.161	(Khalil et al., 2018) (Baderna et al., 2011) (Reis et al., 2017)

The high concentration of EDCs identified in the SLL suggests the potential contamination of SLL if it would be discharged into the environment without adequate treatment.

The elevated number of studies which identified BPA in SLL (Table 2) can be explained by the fact that BPA is used as an additive in polyvinyl chloride, epoxy resins and other plastic products including plastic water bottles, food containers, water pipes, medical equipment, dental sealants, thermal receipts, electronics or toys (Canle et al., 2017). Because of its less hydrophobic characteristic, it tends to leach from the plastic wastes and easily move to the SLL (Asakura et al., 2004; Yi et al., 2017).

Phthalates such as DBP, DEHP, DEP, BBP, DOP, DMP, DiBP are ubiquitous in daily necessities products since they are employed to provide flexibility to rigid polymers. They are also used in paper and paperboard manufacturing as defoaming agents, in capacitors as dielectrics, as food preservatives, in detergents, as insect repellent, plastic, and cosmetics (Bertanza and Pedrazzani, 2007). DiBP is a substitute for di-n-butylphthalate (DnBP) and both are banned in personal care products in the United States and Europe, and in cosmetics due to their classification as the adverse effect on the reproductive system (Lorber and Koch, 2013). The tendency of these compounds to persist in the environment and bioaccumulate in organisms poses its biosafety risks. Besides that, PAEs are almost insoluble in water, however, in the SLL they can be solubilized by interaction with fulvic and humic acids (Bertanza and Pedrazzani, 2007).

According to Canle et al. (2017) and Slack et al. (2005), NP is a surfactant used as an emulsifier in cleansing agents, agricultural chemicals, plastic polymerization processes, dust-control agents and de-icers and these authors indicate photo-assisted electrochemical oxidation (PEO) as the best treatment of wastewater containing NP.

4OP belongs to the alkylphenolic compounds family that is employed as an intermediate product of octylphenol polyethoxylates and phenol/formaldehyde resins production which are used as surfactants (Lin et al., 2019). 4OP nonionic surfactants are used in detergents, pesticide formulations, and other applications such as in plastics and as emulsifiers (Ying et al., 2002). Therefore, the exposure to this compound is related to the contact with personal care products, detergents, water, and food containing 4OP. DTBP also belong to the alkylphenol's group and is widely used as a raw material for polymerization, as well as an inhibitor and stabilizing agent in the chemical industry (Wu et al., 2016).

The recalcitrance of many organic compounds present in complex wastewaters and its persistence through conventional water and wastewater treatment implies in adverse impacts for many communities, especially those who are implementing strategies to reuse municipal wastewater for potable and nonpotable uses. Therefore, the presence of chemicals in SLL demonstrate that this is an issue requiring further attention (Clarke et al., 2015).

3.3. ADVERSE IMPACTS OF EDCS

Concerning the impacts on aquatic life, SLL is very toxic to fishes. Baderna et al. (2011) reported it is able to induce anomalies, DNA damage, developmental disorder and mortality in larval and adult fish at very low doses. Bertanza and Pedrazzani, (2007) explained that most of the EDCs are dangerous for fishes and mammals because they are significant hydrophobic (they can accumulate in fat tissues), but at the same time the extent of their hydrophobicity does not prevent their transfer into aqueous media (e.g. blood) thus their mobility within an organism.

Even at trace level, EDCs present carcinogenic potential and are able to impair the function of hormones in the human body (Asakura et al., 2004; Hong et al., 2017). Besides that, the health risks are not limited to drinking water, since the skin can absorb this compounds and offer the biomagnification effect, increasing its concentration at a successive level in a food chain (Bertanza and Pedrazzani, 2007; James, 1977; Khalil et al., 2018).

In human bodies the endocrine system is responsible for the regulation of metabolic processes, including digestive, cardiovascular and kidney function, bone growth and response to stress (Endocrine Society, 2019), therefore, disorders on this system might end in disease (Canle et al., 2017). The alteration of the endocrine system by chemicals is caused by removing or binding endogenous hormone-receptors, since the EDCs act by mimicking naturally occurring hormones in the body, which in turns may modify processes like synthesis, storage, release, metabolism and transport eliciting any hormonal process at the wrong time (Canle et al., 2017; Kabir et al., 2015; Yang et al., 2015).

In this way, EDCs can be the source of many adverse effects on human bodies. EDCs can be accumulated and transferred from the mother to the fetus (Asakura et al., 2004), as a consequence they can promote congenital malformations in children, retarded sexual development and retarded neurobehavioural development (Canle et al., 2017; Endocrine Society, 2019).

Reduction of fertility, alteration of reproductive and immune functions, an increase in the incidence of breast, ovarian, testicular and thyroid cancer and neurodevelopmental delays also can be cited as consequences to EDC exposure (Bergman et al., 2013; Colborn et al., 1993; Monneret, 2017). Figure 1 presents the main human systems and organs affected by EDCs prolonged contact.

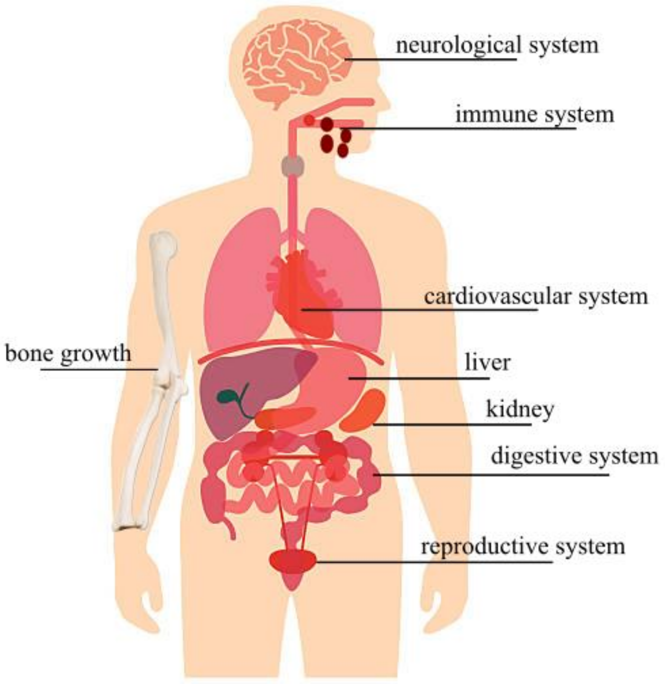


Figure 1. Main human systems and organs affected by contact with EDCs.

Some of the compounds classified as EDCs found in SLL have been studied regarding their adverse effects in human health.

BPA can lead to negative effects in the human body, especially in the early development stages, since it mimics human hormone estrogen (Baderna et al., 2011; Beronius et al., 2010; Canle et al., 2017). Furthermore, the exposure to BPA has been related to higher levels of anxiety, depression, hyperactivity, inattention, and conduct problems in the child (Canle et al., 2017).

PAEs, such as DiBP, are associated with negative effects on the male reproductive system (Borch et al. 2006). Also, PAEs with a linear portion of C4-C6 carbons in their alkyl side chains have been associated with severe developmental and male reproductive effects, examples of such PAEs are DBP, DnHP, and DEHP (Clewell et al., 2013; Gray et al., 2000; Hannas et al., 2011; Willoughby et al., 2000).

DTBP, which belongs to the alkylphenols group is difficult to biodegrade and presents high estrogenic effects and toxic effects at lower concentrations (Barse et al., 2006; Haavisto et al., 2003). Furthermore, DTBP may is related to skin diseases (Manga et al., 2006). Although alkylphenols such as 4OP are considered weak estrogen mimic compounds, they offer risks since they are classified as EDCs and can bioaccumulate in aquatic organisms (Ying, 2006). Qin et al. (2013) studied the exposure of Han-Chinese population to 4-tert-octylphenol and identified an increase in the male infertile risk.

Therefore, the presence and persistence of these compounds poses biosafety risks not just for animals, but also risks for human health, for this reason, efficient technologies should be applied in order to provide their complete removal/degradation.

3.4. TREATMENTS APPLIED TO SLL

SLL present toxic conditions, thus it has to be treated before discharging into the receiving environment (Gong et al., 2016b). Furthermore, the presence of EDCs in SLL could challenge the capacity of existing treatment methods (Hou et al., 2017). Traditionally, the success of the applied treatment was focused on the disappearance of primary pollutants, however, little attention has been receiving concern with the persistence or limiting the formation of organic intermediates, which may be more harmful than primary pollutants (Pahigian and Zuo, 2018), since classical WWTP are not projected to remove organic micropollutants, resulting in its detection in the environment (Rozas et al., 2016).

The main conventional treatments applied aiming the removal of EDCs from SLL include biological treatment (Coors et al., 2003; Fang et al., 2009; Pesci Pereira et al., 2018; Yi et al., 2017), coagulation/flocculation/sedimentation (Asakura et al., 2004; Turki et al., 2013; Zheng et al., 2009), activated carbon (Asakura and Matsuto, 2009) and membrane bioreactor (Boonnorat et al., 2016; Fudala-Ksiazek et al., 2018a; Reis et al., 2017).

Pesci Pereira et al. (2018) reported that a biological treatment had a good performance in the removal of estrogenic compounds, but the estrogenic activity was not completely eliminated after the biological process. On the other hand, Widziewicz et al. (2012) reported that the refractory organic content and the high levels of ammonical nitrogen became the SLL resistant to the biological treatment process.

Considering the fact that EDCs, like BPA and PAEs, are hydrophobic organic compounds, techniques such as adsorption on activated sludge flocs and biodegradation are believed to be the principal means for their removal, as suggested by Fudala-Ksiazek et al. (2018a). These authors reported that a system composed by membrane bioreactor and ultra-filtration was able to remove PAEs and lead to BPA concentration decreasing during the 1st and 2nd phase of the experiment and it generally remained below the quantification limit. Although the treatment strategy demonstrates high efficiency, the authors reported that activated sludge microorganisms might require some time to adapt and effectively biodegrade BPA. On the other hand, according to Asakura and Matsuto, (2009), the adsorption of BPA is possibly inhibited by the preferential adsorption of humic substances present in SLL. Therefore, the high efficiency of these processes may be closely related to the SLL characteristics.

Zheng et al. (2009) reported that a single coagulation/flocculation treatment step was not enough to remove PAEs from SLL since the removal rates were no more than 32%. These findings are in agreement with those reported by Turki et al. (2013), which detected BPA after the coagulation/flocculation treatment and identified only a slow decrease of all predominant compounds found in the raw SLL and Asakura et al. (2004) which could not remove DEHP after an aeration, coagulating sedimentation, and biological treatment. Therefore, an additional treatment step was suggested in order to remove persistent compounds.

In this way, the major challenges in water and wastewater treatment technologies are the removal of pollutants which are refractory to conventional treatment methods (Canle et al., 2017) and its complete mineralization or transformation into harmless organic species (Pahigian and Zuo, 2018).

As a promising treatment technology, advanced oxidation processes (AOPs) and electrochemical advanced oxidation processes (EAOPs) have been demonstrated to be feasible solutions to treatment of SLL, since it could achieve the removal and mineralization of refractory organic matter (Fernandes et al., 2015a; Mandal et al., 2017), inorganic ions (Deng et al., 2018) and EDCs (Seibert et al., 2019; Wang et al., 2010) due to its non-selective oxidation performed by $^{\bullet}OH$.

Processes derived from Fenton's reaction have been widely used for SLL treatment (Borba et al., 2019; He et al., 2009; Seibert et al., 2017, 2019). These processes are based on the catalytic decomposition of hydrogen peroxide by ferrous ion to generate $^{\bullet}OH$, which is able to promote the oxidation of refractory organic compounds, with moderate cost and simplicity of operation (Deng and Englehardt, 2006; Kurniawan et al., 2006; Li et al., 2016a). Among the compounds degraded by the free radicals generated during Fenton's reaction, EDCs including PAEs (Garcia-Segura et al., 2013) can be cited. In this process, $^{\bullet}OH$ reacts fast and unselectively with chemical species in the solution via radical addition, hydrogen abstraction or electron transfer mechanisms and besides the $^{\bullet}OH$ production, other oxidizing species could participate in the EDCs degradation, transforming them into by-products through intermediate compounds ending up in complete mineralization (CO_2, H_2O, and inorganic salts if EDCs contain heteroatoms other than O) in the most favorable cases (Canle et al., 2017; Pignatello et al., 2006).

Although the dissolved organic matter present in SLL may offer protective sorption sites for the contaminant and acts as an $^{\bullet}OH$ scavenging (Pignatello et al., 2006), Asakura and Matsuto, (2009) suggested that only an AOP with the addition of O_3 and H_2O_2 could decrease the concentration of DEHP in an SLL treatment. In this regard, the efficiency of Fenton process was attributed to the removal of organic matter with large molecular weight (such as humic acids) and PAEs with a longer chain, since this process transforms large molecules in smaller ones (He et al., 2009, 2015; Yoon et al., 1998).

The feasibility of Fenton's process can be enhanced with the UV light, due to the photolysis of H_2O_2 molecule which produces extra $^{\bullet}OH$ and due to iron photoactive species which participate in the pollutants removal (Deng and Englehardt, 2006; Monteil et al., 2018; Radha and Sirisha, 2018). Studies affirmed that the UV radiation (photo-Fenton process) could enhance the $^{\bullet}OH$ production when compared to the Fenton process, making possible to oxidize almost all organic compounds in an SLL (Hu et al., 2011; Liu et al., 2014).

The photo-Fenton process reduced NP and BPA from an SLL to under the detection limit and comparing the Fenton and photo-Fenton process, the photo-assisted process promoted the highest removal efficiency. Also, the treated samples showed no genotoxicity (Wang et al., 2016b). Similar results were reported by Hong et al. (2017), who compared the genotoxicity of untreated membrane concentrate and concentrates treated with UV-Fenton, Fenton or activated carbon adsorption processes, where no acute toxicity effect on *Daphina magna* after 120 minutes of photo-Fenton process was detected. Also, photo-Fenton process had the highest efficiency of genotoxic matter removal, being the only studied treatment which showed no obvious genotoxicity.

The improvement in $^{\bullet}OH$ production in the photo-assisted process also can decrease the treatment time. Wang et al. (2016a) reduced the estrogenic potential of treated concentrated leachate expressed as 17β-estradiol equivalent concentrations after 30 minutes of the photo-Fenton process while the Fenton process took 120 minutes for a similar result. Thereby, it can be confirmed that the photo-Fenton process is more efficient in removing compounds with genotoxic potential (Baderna et al., 2019).

Although these processes present high removal efficiency, the quality and toxicity of the formed by-products should be evaluated, mainly due to the fact that when the EDCs are transformed into intermediates or mixed with other compounds, the measured concentration did not represent the estrogenicity correctly (Hou et al., 2017). In this regard, degradation mechanisms and generated by-products should be studied.

3.5. EDCS DEGRADATION PATHWAY BY FENTON'S BASED PROCESSES

Hydroxyl radicals ($^{\bullet}OH$) are the species which cause changes in the structure of organic compounds since they promote the oxidation of recalcitrant organic substances present in raw SLL (Ramírez-Sosa et al., 2013). In Fenton's reaction, they are produced by combining a Fe(II) salt with H_2O_2 in acid media (Fenton, 1894; Pignatello et al., 2006). The $^{\bullet}OH$ reacts with organic compounds mainly by abstracting H from CH, NH, or OH bonds and adding to CC bonds, or adding to aromatic rings (Buxton et al., 1988). Mineralization to CO_2, H_2O, and (if the contaminant contains heteroatoms) inorganic acids can be reached if the intermediates formed further react with $^{\bullet}OH$ and oxygen (Pignatello et al., 2006).

At the end of the Fenton process, low-molecular-weight acids such as glyoxylic, maleic, oxalic, acetic, and formic acids can be formed. This can be explained by the weakly reactive of this acid toward $^{\bullet}OH$. However, in photo-assisted Fenton reaction, these acids may be mineralized via Fe(III)-catalyzed photoreactions. This reduced iron reacts with H_2O_2 producing $^{\bullet}OH$, originating iron photo-active species ($Fe(OH)^{2+}$) which aid in the pollutants removal (Pignatello et al., 2006).

According to Xiao et al. (2013), carboxylic acids like oxalic and butanoic can be generated and further oxidized to saturated alkanes in electro-oxidative processes. This was explained by above-mentioned authors, which reported that the decarboxylation of carboxyl groups took place since the central carbon atom of the functional group is sp^2 hybridized and can be oxidized to a more stable sp hybridized structure CO_2, therefore, the long chain carboxylic acids could be oxidized to saturated alkanes. The generated alkanes can be employed as the carbon source to promote the growth and reproduction of microbial communities, indicating the increase in the biodegradability of the SLL after the oxidative process (Deng et al., 2018). Several studies bring that after an oxidative process the large molecular weight compounds were transformed into small molecular weight organic matter, for example, the degradation of humic substances into small molecular humic compounds (fulvic and ulmic acid), formation and posterior removal of aliphatics during the oxidative process and the conversion of small molecular humic compounds into protein-like substances (lipid, protein, and carbohydrate) (Deng et al., 2018; He et al., 2015).

Even when pollutants that present estrogenic activity are bounded to suspended matter in the raw SLL (Coors et al., 2003), the $^{\bullet}OH$ are able to oxidize both of them considering the fact they are non-selective oxidant (Seibert et al., 2019).

Regarding the removal of EDCs from SLL by AOPs, its efficiency is intrinsically related to the dissolved organic matter and the structure of EDCs (He et al., 2009). Besides that, the solution pH also plays an important role in these processes, since the low pH range employed in oxidative processes like the ones derived from Fenton's reaction make the functional groups of the dissolved organic matter present in SLL dissociate and remain suspended in solution, which in turns give the opportunity of EDCs being sorbed on the dissolved organic matter (He et al., 2009; Lau et al., 2001).

Although after oxidative treatment processes the samples did not present acute toxicity, toxic compounds can still be present, and according to Reis et al. (2017) this can be explained by three hypotheses: i) the concentration of the toxic substance is very low, thus do not provide toxic effects; ii) the interaction of the toxic substance with other compounds present in the solution eliminates the toxicity of the wastewater as a whole; iii) the compound presents chronic toxicity, which is not detected by tests of acute toxicity.

On the other hand, treated samples can be more refractory and have a higher estrogenicity activity than the raw samples, thus this can be related by the formation of intermediates during the oxidative process (Hong et al., 2017). Hou et al. (2017) identified higher estrogenic effect after an UV-Fenton process, which was ascribed by the presence of phthalic acid esters in the SLL treated samples. Therefore the presence of these compounds after the oxidative treatment is a concern around the safety of the treated samples. In this view, the study of degradation pathway can be useful to predict the efficiency and security of the treatment step, as well as the treatment duration required to reach standard discharge parameters and a non-toxic effluent.

There still is a lack on studies which investigate the degradation pathways of EDCs in SLL, since this wastewater is a complex matrix and several factors may interfere on the degradation process and the synergy among the different compounds present in the SLL increase the difficulty of predict how the EDCs will be degraded. Nevertheless, there are studies that assess the degradation pathways of EDCs by •OH in synthetic solutions, performed with different AOPs, that can be used as reference for future studies applying Fenton-based processes to SLL (Serra-Pérez et al., 2019; Sharma et al., 2015; Wang et al., 2010; Wu et al., 2016; Zhao et al., 2018).

Wu et al. (2016) affirmed that the degradation pathway of PAEs includes the attack of the side chain by $^\bullet$OH followed by the breakdown of the benzene ring. In a study where the mentioned authors investigate the DBP degradation by a photochemical process with H_2O_2 addition to produce $^\bullet$OH, after a long irradiation time, the benzene ring of DBP was fractured and as a consequence alcohols and ketones were produced. Hydroquinone and 4-tert-butylcatechol were produced by $^\bullet$OH attack on the benzene ring and the carbon double bound of tert-butyl and 4-tert-butylphenol dimer was produced by the direct photolysis of the solution as a result of photopolymerization.

Wang et al. (2010) studied the DEP degradation by an electro-oxidative process which led to monoethyl phthalate, phthalic acid and aliphatic intermediates such as formic, mesoxalic, oxalic, malonic, succinic, maleic, dodecanoic, and hexadecanoic acids, that were transformed to carbon dioxide and water after 6 hours of treatment. The proposed degradation pathway includes sequential oxidation breakage of both ester groups of the phthalate (originating monoethyl phthalate and phthalic acid by the removal of the second ethyl group). The attack of $^\bullet$OH led to aliphatic carboxylic acids production after opening the ring of phthalic acid until the final products which were carbon dioxide and water. Similar findings were reported by Xu et al. (2007), which deduced that in the photochemical degradation of DEP the aliphatic chain cracked was followed by the ring decomposition.

Therefore, it can be inferred that AOPs are efficient alternatives to degrade/mineralize PAEs. Nonetheless the treatment duration is a key factor in order to achieve treated solution without a biosafety risk, since the $^\bullet$OH attack starts on side chain, such as esters groups, as a consequence originating aliphatic compounds which usually are removed during the oxidative process, spreading to the breakdown of the benzene ring upon a certain $^\bullet$OH attack period. Also verified by Hong et al. (2017) the lack of treatment time might lead to the remaining of PAEs in SLL solutions resulting in a further estrogenic activity. In this regard, the estrogenic effects of a solution containing 4OP probably disappeared after the breakdown of the benzene ring explained by the vanish of phenol groups which exhibited estrogenic properties (Yamazaki et al., 2008).

Regarding the oxidation of surfactants by Fenton process, the reaction pathway consisted of the $^{\bullet}OH$ attacking the alkyl chain, which led to the abstraction of hydrogen and insertion of oxygen atoms, as a consequence water-soluble compounds containing hydroxyl or epoxide groups were formed (Cuzzola et al., 2000). It has been suggested by the previously mentioned authors that the main volatile oxidation intermediates were linear aliphatic aldehydes that probably derived from the breakdown of ether bond between ethoxylic and hydrocarbon chains.

The radicals $^{\bullet}OH$ can easily attack the symmetrical phenyl rings in BPA degradation (Zhao et al., 2018), cracking the bond between two aromatic rings forming phenol and 4-isopropylphenol (Jamil et al., 2017). The opening of the aromatic ring and the formation of inorganic acids was evidenced by the increase of inorganic carbon (Young et al., 2013). Sharma et al. (2015) related this to the fact that solution pH decreases during the oxidation period, which was supported by the formation of aliphatic acids and aldehydes as a product of aromatic intermediates formed by the $^{\bullet}OH$ and SO_4 radicals attack. Therefore, $^{\bullet}OH$ was mainly responsible for the degradation of BPA in a UV/H_2O_2 process that started with the attack of hydroxyl radical to electron rich position (Sharma et al., 2016).

Serra-Pérez et al. (2019) proposed the following BPA degradation pathway: $^{\bullet}OH$ attack of the electrophilic group on the aromatic ring of BPA that occurred at ortho-position due to the orientation effects in substituted biphenols. Then electrophilic substitution of the hydrogen located on C2 or C4 positions took place, followed by reactions such as radical coupling, fragmentation, substitution and elimination which led to phenolic and quinone groups generation. As long as the oxidative process proceeds, the intermediate products can be converted to carboxylic acids molecules such as hexadecanoic acid, formic acid, acetic acid, maleic acid, since compounds like quinones are readily attacked by $^{\bullet}OH$ (Jamil et al., 2017; Pignatello et al., 2006; Zhao et al., 2018).

In a study performed by Xiao et al. (2013), an SLL was treated by an electrochemical process combined with UV irradiation, where carboxylic acids (such as oxalic, butanoic, benzoic and phenylacetic acids) were identified by GC-MS analysis at the end of the process. Therefore, the proposed pathway mechanisms tested by synthetic solutions may be applicable to predict the behavior of EDCs oxidized by $^{\bullet}OH$ in an SLL matrix.

Although $^{\bullet}OH$ may provide toxicological safety in wastewater treatment (Wang et al., 2016a), the cost of treatment until mineralization is significantly high (Hou et al., 2017; Oulego et al., 2016). On the other hand, since AOPs are able to convert refractory organic compounds into biodegradable organic compounds, it is not necessary to degrade the pollutants to the final products. Thus these processes can be employed to transform refractory organic compounds into pre-degraded compounds which, can be used as carbon source by microorganisms, as example aliphatic carboxylic acids and alkanes (Deng et al., 2018; Wang et al., 2010), improving biological reactors efficiency (Castillo-Suárez et al., 2019). Therefore the integration of oxidative process with biological system is a worthwhile alternative in order to obtain economical and safe treated samples.

3.6. COMBINED SLL TREATMENTS

Although biological processes are widely applied to SLL treatment due to its low cost and easy operation, wastewater like SLL usually present compounds that are recalcitrant, inhibitory, or toxic in biological treatment steps, such as humic and fulvic acids which are heterogeneous complexes, consisting of functional groups formed by the biogeochemistry processes (Mandal et al., 2017; Xi et al., 2016). Therefore, combined treatment processes can be employed to overcome this inconvenient. Integration of Fenton based processes and biological process as a pretreatment or post-treatment step for SLL treatment have shown promising results (Klein et al., 2017; Mandal et al., 2017; Seibert et al., 2019; Silva et al., 2013). This integration of treatments refers to the expectation that the parent molecule is usually more reactive chemically than biologically, and depending on the treatment strategy the opposite is also true (Pignatello et al., 2006). Therefore the combination of these AOPs with other treatment techniques have been applied to prevent the release of micro-pollutants via wastewater discharge (Boonnorat et al., 2016).

Regarding on the strategy of combined treatment, biological oxidation aiming the reduction of biodegradable organic load followed by AOPs adopted as post-treatment to remove remaining recalcitrant organic matter is the approach most reported in the literature (Mandal et al., 2017). Nevertheless Seibert et al.

(2019) identified that in a non-biodegradable SLL (BOD_5/COD=0.18) treatment, the application of a photo-electro-Fenton process followed by a biological oxidation was the most suitable treatment strategy, since the recalcitrant organic compounds were converted to more biodegradable ones including the degradation of EDCs by $^{\bullet}OH$, enabling the posterior biological process. The opposite strategy (biological process followed by photo-electro-Fenton process) was not as efficient as the Fenton based process applied as pre-treatment, probably because microbial cultures acted as an $^{\bullet}OH$ scavenger reducing its removal efficiency. Similar findings were reported by Baiju et al. (2018) that pursue a subsequent biological treatment since the application of electro-Fenton as standalone treatment did not meet the wastewater discharge standards. However, the electro-Fenton improved the biodegradability of SLL (DOB_5/COD of 0.03 to 0.40) which was attributed to organic pollutants oxidized to biodegradable intermediates by $^{\bullet}OH$. The combined process provided 97% of COD removal, while the electro-Fenton as standalone step reached 82% of COD removal. Colombo et al. (2019) met the Brazilian wastewater standard discharge for COD and BOD_5 parameters by the combination of photo-Fenton and biological processes where removal rates of 98% of COD and 98% of BOD were reached. Besides that, good removal rates were found for single and conjugated aromatic compounds (~93 and 96%), color and turbidity (98%) and a reduction in the residual amount of sludge was observed in the combined treatment. As a suggestion, a complementary anaerobic/anoxic treatment should be performed to reach the nitrogen, phosphorus, and sulfate discharge levels imposed by legislation.

The conversion of recalcitrant organic compounds into biodegradable ones promoted by AOPs also was evidenciaded by Deng et al. (2018) which increased the number of organic substances that could be used by microorganisms by destroying humic-like compounds during an electrolysis process applied to SLL treatment. As a result, the BOD_5 increased from 39 to 90 mg L^{-1} during 60-180 minutes. Silva et al. (2013) reported that in a multistage SLL treatment composed by biological – chemical – biological oxidation, the main recalcitrant fraction was attributed to humic substances, representing 57% of DOC. Appling the first biological oxidation, only recalcitrant compounds remained. Then these compounds were removed with the aid of a solar photo-Fenton process (80% of removal), remaining in solution biodegradable compounds which were further degraded in a second biological oxidation. Therefore, this multistage process enabled to achieve legal discharge limits regarding water bodies. These findings are in agreement with Klein et al. (2017) that achieved the removal of recalcitrant organic substances, represented by phenols, lignin and tannin employing a Fenton-like process in a SLL three-stage treatment where, recalcitrant substances were transformed into biodegradable compounds, which were further removed by activated sludge treatment.

de Pauli et al. (2018) performed a biological treatment after 5 minutes of electrocoagulation, which was possible to remove 89% and 95% for the COD and DOC, respectively, in comparison to the single biological treatment that only removed 82% of COD and 75% of DOC. The better results obtained in the in tandem process were confirmed by the improvement in toxicity and ascribed to the hydrolysis of macromolecules (Djelal et al., 2015).

Li et al. (2016a) obtained removal efficiency of 81% for 3-ring PAHs and 90% for 2-ring PAHs by the combination of Fenton oxidative-coagulation with UV-Fenton treatment in the degradation of an SLL. It was presumed that PAHs with more rings were less biodegradable and the degradation of trace organic compounds on the single treatment was decreased by the high dissolved organic matter content in the SLL whereas six phthalic acid esters and thirteen polycyclic aromatic hydrocarbons were detected in the SLL samples. The integration of chemical coagulation and electrochemical oxidation also seems feasible for the treatment of SLL. In this processes, the coagulation reduced organic load and electrochemical oxidation oxidized residual organic matter and nitrogen species (Fernandes et al., 2015b).

In this regard, it can be concluded that combined processes used to provide higher removal rates when compared to standalone ones. Although many kinds of combined processes are studied, conventional biological processes still are considered the cheapest treatment step and its integration with Fenton-based processes have been successfully applied to the SLL treatment in order to reach wastewater discharge standard levels, recalcitrant organic matter and EDCs removal with cost reduction.

3.7. FUTURE RESEARCH NEEDS AND CONCLUSIONS

The detection of EDCs in SLL is increasing concerns about the biosafety risk of the treated samples since these compounds may pass through conventional WWTP and can be released into the environment, undermining the supply of water to all communities. The presence of these compounds in SLL is mainly associated with the disposal and leaching of plastic and personal care products, insecticides and cleaning, and hygiene products in the dumping site. Efficient segregation and recycling policies in the solid waste management system would greatly reduce the release of EDCs on the sanitary landfill sites. Several EDCs were detected in sanitary landfills around the world, highlighting the 12 most frequent which were mainly divided into BPA, PAEs; surfactants: BPA, DBP, DEHP, DEP, NP, BBP, DOP, DMP, 4OP, DiBP, DTBP and nicotine. The exposure to EDCs has been associated with many abnormalities in human and animals, may presenting acute or chronic adverse effects. Although recent research efforts have brought significant progresses towards impacts of EDCs in animals and human health, more studies are suggested in order to advance our understanding around the limiting exposure concentrations and how these compounds behave in animals and humans bodies.

Fenton-based processes have been studied to degrade/mineralize this kind of compounds, therefore, not just the production of the oxidative species ($^{\bullet}OH$) should be taken into account, but also the degradation pathway of EDCs present in SLL by $^{\bullet}OH$ and the intermediates products, since they can be more harmful than parent compounds. In this review a lack of works exploring the degradation pathway of EDCs in a SLL matrix have been evidenced, since only studies regarding the degradation in synthetic solutions were found. As not a widely explored topic, further studies should investigate how the EDCs are degraded in SLL by $^{\bullet}OH$ as well as the synergic effects of a multicomponent matrix aiming to reduce the toxic and estrogenic effects of this wastewater. The safe and environmental friendly disposal of iron sludge and the handle of the chemical solution wastes are not completely addressed. Therefore, more reasearches needs to be accomplished in this field.

Regarding the effectiveness and cost reduction of SLL treatments, the combined strategy have been employed. Although many attempts have been made in order to reduce the SLL treatment costs, more researches are needed to elucidate the economic aspect of standalone and/or combined treatment strategies to encourage the real-life application on the industrial use of the novelty techniques being study in bench scale. Among the most commom integrated system, Fenton-based processes with biological oxidation can be cited. Thus, according to recent research, it was more suitable to apply AOPs as a pre-treatment aiming to transform recalcitrant organic matter in biodegradable compounds, reducing the SLL toxicity and enabling the posterior biological oxidation.

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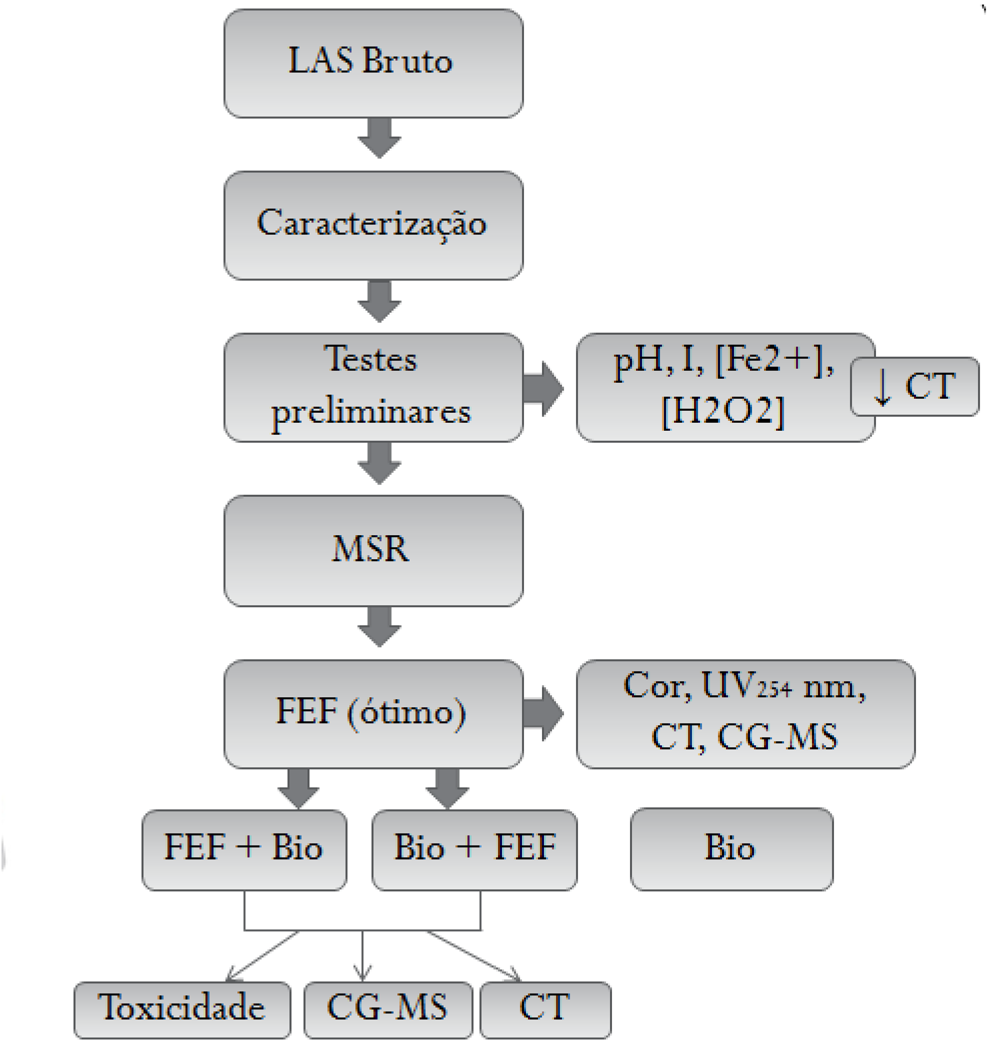
[redacted]4. METODOLOGIA EXPERIMENTAL

O fluxograma a seguir apresenta um esquema quanto à organização do presente trabalho.



4.1. AMOSTRAS, SOLVENTES E REAGENTES

As amostras de LAS foram coletadas em uma Central de Tratamento de resíduos sólidos urbanos localizada no noroeste do Estado do Rio Grande do Sul – Brasil (latitude: -28º, longitude: -54º). Este efluente foi coletado no tanque de equalização em 27/02/2018 e encontra-se estocado de acordo com Standard Methods (APHA; AWWA; WEF, 2005). O aterro sanitário em questão recebe apenas material orgânico, sendo este disposto em células impermeabilizadas e com coleta de efluentes líquidos e gasosos. Reagentes de pureza analítica serão utilizados em todos os experimentos. Água destilada será produzida por Millipore Direct-Ultrapure (MilliQ®). Ácido sulfúrico (Vetec, 1,5 M) será empregado para o ajuste de pH, peróxido de hidrogênio (H_2O_2) (ALPHATEC, 35%) e sulfato de ferro heptahidratado ($FeSO_4 \cdot 7H_2O$, Vetec) serão empregados como reagentes Fenton. O_2 será promovido à solução através de um cilindro conectado a um rotâmetro ao fluxo de 3,2 L min^{-1}.

O lodo ativado a ser empregado no tratamento biológico do LAS será coletado em uma estação de tratamento de efluentes de uma empresa de processamento de produtos alimentícios, localizado no Oeste do estado do Paraná – Brasil (latitude: -24º, longitude: -53º).

Os cistos de *Artemia Salina* foram adquiridos de Maramarpet e para preparação da solução de Meyer, 23,0 g de NaCl, 11,0 g de $MgCl_2.6H_2O$, 4,0 de Na_2SO_4, 1,3 g de $CaCl_2.2H_2O$ e 0,7 g de KCl serão colocados em um balão volumétrico de 1,0 L cujo volume será completado com água Milli-Q, pH 9,0 será empregado onde o ajuste de pH será realizado com Na_2CO_3 (MEYER et al., 1982, p. 19).

Para os testes de Zahn Wellens serão utilizados fosfato monopotássico (KH_2PO_4), potássio dibásico fosfato (K_2HPO_4), fosfato dissódico (Na_2HPO_4), cloreto de amónio (NH_4Cl), cloreto de cálcio ($CaCl_2$), sulfato de magnésio ($MgSO_4$), cloreto de ferro ($FeCl_3$) e glicose ($C_6H_{12}O_6$) (OECD, 1992).

4.2. DETERMINAÇÕES ANALÍTICAS

A Tabela 1 apresenta as determinações analíticas que foram empregadas nos experimentos realizados e as mesmas metodologias de determinações serão empregadas nos testes subsequentes.

Tabela 1. Metodologias e equipamento empregados nas determinações analíticas.

Parâmetro	**Metodologia/Equipamento**	**Referência**

H_2O_2	Método de metavanadato/ Espectrofotômetro UV-vis (Evolution 201/220 – Thermo 168 Scientific)	NOGUEIRA; OLIVEIRA; PATERLINI, (2005)
Cor	Método de Pt-Co/ Espectrofotômetro UV-vis (Evolution 201/220 – Thermo 168 Scientific)	(APHA; AWWA; WEF, 2005)
UV_{254nm}	Espectrofotômetro UV-vis (Evolution 201/220 – Thermo 168 Scientific)	DIA et al. (2017)
pH, temperatura	pHmetro (HANNA, HI 3221)	
Turbidez	Turbidímetro (PoliControl, AP 2000 iR)	
Condutividade	Condutivímetro (Digimed, DM-32)	
CT, NT	Analisador TOC (Shimadzu, TOC-L series)	
COD	Analisador de carbono orgânico total (Shimadzu, modelo TOC-VCPH).	
DBO_5	Protocolo OECD-301F OECD-301F - sistema OxiTop (respirometria manométrica)	(APHA; AWWA; WEF, 2005)
DQO	Método colorimétrico de refluxo fechado	(APHA; AWWA; WEF, 2005)
ST, SS, SV, SF	Métodos gravimétricos	(APHA; AWWA; WEF, 2005)
Ferro total	Fluorescência de raio-X por reflexão total (TXRF) (S2 PICOFOX, Bruker AXS Microanalysis GmbH)	ESPINOZA-QUIÑONES et al. (2015).

Análises de cromatografia a gás e espectrometria de massa (GC-MS)	GCMS-QP2010 (SHIMADZU, Japão).

As concentrações de H_2O_2 foram determinadas pelo método de metavanadato de amônio descrito por NOGUEIRA; OLIVEIRA; PATERLINI, (2005). Este método baseia-se na formação de um cátion de cor vermelho-alaranjado quando o peróxido reage com o metavanadato. A absorbância do H_2O_2 é detectada por espectrofotometria a 450 nm.

A cor foi expressa em unidades de Pt-Co em diluição de 1:25 e determinada de acordo com Standard Methods (APHA; AWWA; WEF, 2005) mensurada através da leitura no comprimento de onda de 455 nm (Evolution 201/220 – Thermo 168 Scientific).

Um espectrofotômetro UV-vis (Evolution 201/220 – Thermo 168 Scientific) foi utilizado para mensurar o comprimento de onda de compostos aromáticos simples (254 nm) como forma qualitativa rápida e simples com o objetivo de exibir uma queda nesta faixa típica de absorbância relacionada ao grupo funcional orgânico tóxico.

O pH da solução foi aferido e monitorado durante as reações de FEF por um pHmetro (HANNA, HI 3221), equipamento também utilizado para medição da temperatura. A turbidez das amostras foi medida utilizando um turbidímetro (PoliControl, AP 2000 iR), expressa em NTU. A condutividade foi determinada através do uso de um condutivímetro (Digimed, DM-32).

Carbono total (CT), carbono inorgânico (CI), nitrogênio total (NT) e carbono orgânico (CO) foram mensurados por um analisador TOC (Shimadzu, TOC-L series) que é baseado no método de oxidação catalítica de combustão (680 ºC) e para estimar o CT das amostras centrifugadas tratadas e não tratadas um limite de detecção de 4 $\mu g\ L^{-1}$ foi aplicado.

O carbono orgânico dissolvido (COD), o qual é uma subtração do carbono total dissolvido (CTD) do carbono inorgânico dissolvido (CID), bem como o nitrogênio total serão determinados utilizando um analisador de carbono orgânico total (Shimadzu, modelo TOC-VCPH).

DBO_5 foi determinada de acordo com protocolo OECD-301F OECD-301F utilizando um sistema OxiTop (respirometria manométrica), conforme descrito no Standard Methods (APHA; AWWA; WEF, 2005). DQO foi determinada pelo método colorimétrico de refluxo fechado. Esta metodologia foi realizada em quintuplicata utilizando uma solução estoque Combicheck 20 com 750 ± 75 mg O_2 L^{-1}, obtendo-se um resultado médio de 742 ± 12.3 mg O_2 L^{-1} (APHA; AWWA; WEF, 2005).

Os sólidos totais (ST), suspensos (SS), voláteis (SV) e fixos (SF) foram determinados utilizando métodos gravimétricos segundo o (APHA; AWWA; WEF, 2005).

A concentração de ferro total em solução foi analisada por fluorescência de raio-X por reflexão total (TXRF) (S2 PICOFOX, Bruker AXS Microanalysis GmbH) de acordo com metodologia descrita por ESPINOZA-QUIÑONES et al. (2015). Para a análise no TXRF as amostras serão dispostas em discos de quartzo previamente preparados para receber as amostras de LAS. A preparação dos discos de quartzo envolve a limpeza com álcool isopropílico, aquecimento em solução de RBS 5% durante meia hora, enxague com água ultra pura Milli-Q, repouso em solução de ácido nítrico 10% sob aquecimento durante duas horas, novo enxague com água ultra pura Milli-Q e aquecimento na água durante meia hora. Após este procedimento, os discos secarão a temperatura ambiente em capela de fluxo laminar durante 24 horas. As amostras de LAS serão preparadas com 950 µL de amostra e 50 µL do padrão interno Gálio, totalizando uma concentração de 50 ppm do padrão interno Gálio. Após homogeneização da amostra, 5 µL serão inseridos nos discos de quartzo para análise no equipamento.

Um processo de extração baseado em CH_2Cl_2 (3x20 mL) foi previamente realizado em 40 mL de amostras de LAS tratadas e não tratadas. Após a extração, a camada orgânica combinada, foi seca com $MgSO_4$ anidro e concentrada por rota evaporação a 40 °C. Análises de cromatografia a gás e espectrometria de massa (GC-MS) foram realizadas empregando o equipamento GCMS-QP2010 (SHIMADZU, Japão), equipado com uma coluna NST 05 MS (30 m, 0.25 mm, 0.25 µm espessura do revestimento) que foi composta de dimetilpolissiloxeno (95%) e difenil (5%). O injetor e detector de temperatura foram configurados 280 °C, com temperatura de interface de 200 °C. Para cada amostra de 1µL foi realizada uma injeção com uma razão de separação de 1:10 He gasoso e uma taxa de fluxo de 1,65 mL min^{-1}. A temperatura inicial no equipamento, foi ajustada para 50 ºC, mantida constante por 7 minutos, com aumento de 25 ºC min^{-1} até 280 ºC e mantida por 20 minutos. A voltagem do equipamento de CG-MS foi configurada a 0,88 kV, que promoveu uma ionização por impacto de elétrons de 70 eV permitindo a fragmentação molecular e produção de íons em um campo de massa/carga elétrica (m/z) de 25 a 500, possibilitando determinar as concentrações de subprodutos nas amostras e identificar suas estruturas. A temperatura da fonte de íons foi mantida fixa a 250 °C para selecionar e quantificar os compostos orgânicos nas amostras. Um conjunto de compostos orgânicos em relação a m/z foi comparativamente identificado com base em seus padrões característicos de GC-MS usando a biblioteca NIST 08 disponível no GCMS-QP2010.

4.2.1. Testes de toxicidade

Testes de toxicidade serão realizados utilizando *Artemia Salina* cuja metodologia é descrita por Meyer et al. (1982) onde uma solução nutriente – denominada solução de Meyer será preparada. Os cistos serão colocados na solução de Meyer para eclodir após 48 horas, e o recipiente será dividido por uma folha de transparência perfurada, onde apenas as larvas que migraram para o lado claro serão utilizadas por serem consideradas mais resistentes, sendo utilizadas 10 larvas em cada tubo. Diferentes diluições de LAS bruto e tratado serão realizadas em duplicata de 5 mL de amostra. A solução de Meyer será utilizada como solução controle e de diluição. Após 24 horas o número de organismos em cada tubo será medido e a concentração letal ($CL_{50\%}$), que é a concentração de um determinado agente num meio que causa mortalidade em cinquenta por cento (50%) da população exposta, durante um determinado período de tempo, será estimada com auxílio do software Trimmed Spearman-Karber Method, versão 1.5 (HAMILTON; RUSSO; THURSTON, 1977).

4.3. REATOR DE FEF E PROCEDIMENTO EXPERIMENTAL

As reações de FEF foram realizadas em um reator de escala de bancada em sistema batelada em sistema fechado composto por uma caixa com revestimento interno de aço inoxidável (54 x 42 x 62 cm) equipado com duas lâmpadas de mercúrio (Philips 13 W) como fonte de radiação UVC, béquer com capacidade de 1 L e agitador magnético.

Acima do béquer, quatro placas paralelas de ferro fundido (11.9 x 7.0 x 0.2 cm) foram utilizadas como eletrodos (cátodo e ânodo), com espaçamento entre placas de 2,0 cm e área efetiva de 155,22 cm². Eletrodos de BDD também serão empregados para o estudo das reações de FEF. Os eletrodos serão arranjados de forma bipolar em terminais positivos e negativos, conectados a uma fonte de corrente contínua (BK precision/1687B, 20 V maximum voltage, e 10 A direct current) e para apoiar as conexões bipolares, duas barras de aço (2 x 16 cm) serão instaladas como suporte.

As corridas experimentais serão baseadas na adição de 0,8 L de LAS bruto no béquer sob agitação constante de aproximadamente 60 rpm. O pH da solução será ajustado para a condição inicial estabelecida e os reagentes químicos quando necessários serão adicionados à reação. Após, serão iniciados simultaneamente a incidência da radiação, dissipação de uma intensidade de corrente contínua e uma taxa constante de 3,2 L O_2 min^{-1} de oxigênio dissolvido que será fornecido à solução para aumentar o número de radicais livres produzidos, melhorando a eletro-geração de peróxido de hidrogênio (WANG et al., 2005, 2010). Geralmente em processos eletroquímicos formam-se camadas externas nos eletrodos, o que aumentar a resistência do circuito, e por sua vez, diminui a eficiência do processo. Desta forma, após 30 minutos de eletrólise será realizada a inversão de polaridade visando evitar a passivação dos eletrodos (BUENO et al., 2018).

Para o processo FEF com eletrodos de ferro fundido, inicialmente foram realizados testes preliminares do processo FEF variando a intensidade de corrente de 0,5 – 4,0 A, concentração inicial de H_2O_2 de 5000 – 15000 mg L^{-1}, pH inicial de 3,0 – 7,0 e concentração inicial de Fe^{2+} de 0 a 100 mg L^{-1}, em tempos de eletrólises de 5 a 90 min. A redução da concentração inicial de CT e o comportamento do pH da solução e os residuais das concentrações de H_2O_2 e Fe^{2+} foram monitorados para avaliar a performance de eficiência do FEF.

Uma metodologia de superfície de resposta (MSR) foi aplicada para identificar a região ótima das condições experimentais do reator FEF. Baseado no delineamento central composto rotacional (DCCR) foram investigados os parâmetros operacionais, tais como: intensidade de corrente (q_1) (0 – 4,6 A), concentração inicial de H_2O_2 (q_2) (0 – 18000 mg L^{-1}), concentração inicial de Fe^{2+} (q_3) (0 a 120 mg L^{-1}) e tempo de eletrólise (q_4) (15 – 120 min). Nestes experimentos o pH da solução foi controlado na faixa de 3,5 a 4,5, para minimizar os efeitos adversos da instabilidade de H_2O_2 e presença de reações parasitas secundárias (FENG et al., 2003; WANG et al., 2010; WANG; LEMLEY, 2001). Para interpretar os 28 ensaios experimentais (16 pontos fatoriais, 8 pontos axiais e 4 repetições nos pontos centrais) foi considerado um modelo polinomial de segunda ordem (ver Equação 23), que avaliou a qualidade da Equação ajustada pela análise de variância (ANOVA – baseada o *F*-test) e seus efeitos lineares (q_n) e quadráticos (q^n) e suas interações em função da redução da concentração inicial de CT. Os testes estatísticos foram realizados utilizando o software Statistica®. A metodologia detalhada da MSR foi desenvolvida e é reportada por Borba et al. (2018).

$$R = a_0 + \sum_{i=1}^{k} a_i q_i + \sum_{i=1}^{k} a_{ii} q_i^2 + \sum_i i < j \sum_j a_{ij} q_i q_j \qquad (23)$$

Onde R é a variável resposta, q_i e q_j são as variáveis independentes, a_0 é o termo de interceptação, a_j é o coeficiente que determina a influência do parâmetro *i* na resposta (termo linear), e a_{ij} se refere ao efeito de interação.

Baseado na condição experimental ótima do processo FEF foi realizado um estudo detalhado do tempo de eletrólise de 5 a 90 minutos, com retirada de alíquotas em tempos pré-estabelecidos (5, 15, 30, 45, 60 e 90 minutos) visando avaliar a redução da concentração inicial de CT, cor, absorbância em 254 nm e subprodutos intermediários da reação.

Para os experimentos de FEF com eletrodos de BDD, serão aplicadas as condições otimizadas encontradas através do método acima descrito, empregando-se as mesmas condições analíticas.

4.4. REATOR BIOLÓGICO E PROCEDIMENTO EXPERIMENTAL

Em sistemas biológicos de digestão aeróbia, micro-organismos (principalmente bactérias e protozoários) atuam em matéria orgânica dissolvida, coloidal e matéria inorgânica suspensa de efluentes, as transformando em gases e matéria celular que podem ser separadas por sedimentação (CHIAVOLA; FARABEGOLI; ANTONETTI, 2014; ZHOU et al., 2017).

Com o objetivo de avaliar a integração de digestão biológica aeróbia como etapa de pré-tratamento ou de polimento ao processo FEF, testes de oxidação biológica serão realizados em um reator SOLAB, SL-135. O biorreator possui capacidade de 5 L, equipado com um vaso de vidro cilíndrico encamisado, compressor para a entrada de ar, agitador e sensores para aferição do pH e oxigênio dissolvido, conectados a um computador que possibilita o controle automático da aeração, agitação e controle de pH. Para o controle de temperatura, um banho termostático será acoplado ao reator. Os testes de degradação biológica do LAS serão realizados conforme metodologia descrita por De Pauli et al. (2018), onde 3 L da solução serão tratados mediante a adição de inóculo ao biorreator. Uma solução de sulfito de sódio será utilizada para definir as condições de ausência de oxigênio dissolvido, visto que este sequestra moléculas de oxigênio do meio. Agitação de 500 rpm e 2 L min^{-1} de aeração serão empregados. Uma relação de alimento/micro-organismo (F/M) de 1 será utilizada. O pH do meio será mantido em 7,0; a temperatura em 33°C e o oxigênio dissolvido em 50%.

4.5. SISTEMAS INTEGRADOS

O estudo dos sistemas integrados será realizado a partir da condição otimizada do processo FEF onde duas estratégias de tratamento serão investigadas, a aplicação do processo eletro-químico como etapa de pré-tratamento ao processo biológico e o processo eletro-químico como etapa de pós-tratamento ao processo de oxidação biológica.

Para primeira estratégia de tratamento, corridas experimentais de 45 minutos do processo FEF serão realizadas para obter o volume necessário de 3L de LAS tratado que será fornecido ao biorreator que operará durante 24 horas, obtendo-se o resultado do processo intitulado FEF 45 min. + 24 Bio.

Para segunda estratégia de tratamento, primeiramente somente o tratamento biológico do LAS bruto durante 24 horas será realizado, obtendo-se o resultado Bio 24 h. Após, o efluente do Bio 24 h passará por 45 minutos de eletrólise mediante a aplicação do processo FEF nas condições otimizadas, obtendo-se assim o resultado intitulado Bio 24 h + FEF 45 min.

[redacted]5. ARTIGO 2: TWO-STAGE INTEGRATED SYSTEM PHOTO-ELECTRO-FENTON AND BIOLOGICAL OXIDATION PROCESS ASSESSMENT OF SANITARY LANDFILL LEACHATE TREATMENT: AN INTERMEDIATE PRODUCTS STUDY

Em consonância com as normas do Programa de Pós-graduação em Engenharia Química (Resolução nº 057/2020/CTC, Art. 59º), o segundo artigo foi redigido de acordo com as regras da revista Chemical Engineering Journal.

Two-stage integrated system photo-electro-Fenton and biological oxidation process assessment of sanitary landfill leachate treatment: an intermediate products study

Daiana Seibert[1,♣], Fernando Henrique Borba[2,♣], Francine Bueno[2], Jonas J. Inticher[2], Aparecido N. Módenes[3], Fernando R. Espinoza-Quiñones[3], Rosângela Bergamasco[1]

[1] Postgraduate Program of Chemical Engineering, State University of Maringa, UEM, Av. Colombo, 5790, Maringa, Parana, CEP: 87020-900, Brazil

[2] Postgraduate Program of Environment and Sustainable Technologies, Federal University of Fronteira Sul, Rua Jacob Reinaldo Haupenthal 1580, 97900-00, Cerro Largo, RS, Brazil.

[3] Postgraduate Program of Chemical Engineering, West Paraná State University, Rua da Faculdade 645, Jd. Santa Maria, 85903-000, Toledo, PR, Brazil.

♣ Corresponding author

Tel.: +55 (55) 3359 3950, 3971, E-mail: daiaseibert@hotmail.com (Daiana Seibert); fernando.borba@uffs.edu.br (Fernando H. Borba)

Permanent address: Universidade Federal da Fronteira Sul-UFFS, Rua Jacob Reinaldo Haupenthal, 1580, Sala 104, Bloco dos Professores. Bairro Industrial, 97900-00, Cerro Largo, RS, Brazil.

Abstract

Optimum experimental conditions for the photo-electro-Fenton (PEF) process using a lab-scale photo-reactor to treat a sanitary landfill leachate (SLL) were determined. The PEF process operational conditions were analyzed with a response surface methodology (RSM) that presented a high total carbon (TC) removal at the central point: current intensity of 2.3 A, H_2O_2 concentration of 9000 mg·L^{-1}, Fe^{2+} concentration of 60 mg·L^{-1}, an electrolysis time of 45 min and solution pH controlled at the range 3.5 – 4.5, reaching a minimum TC residual concentration of 344 mg·L^{-1} in the SLL, as well as 89 mg Pt-Co·L^{-1} of color, 254 nm = 0.18 a.u., 315 mg·L^{-1} 5th day biochemical oxygen demand (BOD$_5$), 782 mg·L^{-1} chemical oxygen demand (COD), improving the BOD$_5$/COD = 0.4 ratio. The reaction byproducts were analyzed with gas chromatography-mass spectrometry (GC-MS). The generated byproducts were less toxic than the parent compounds found in the raw SLL. As the SLL toxicity was reduced, integration treatment strategies containing PEF processes and biological oxidation (BO) were studied. The best treatment strategy enabled the lethal concentration LC$_{50\%}$ = 33% and reduced the residual TC concentration to 181 mg·L^{-1} through application of the PEF process. This possibly transformed recalcitrant compounds from raw SLL into more biodegradable substances (BOD$_5$/COD = 0.53) facilitating the microbial activity in the posterior BO. This treatment strategy also produced a smaller number of identified byproducts, which confirms the good performance of the PEF process followed by BO.

Keywords: Sanitary landfill leachate; Integrated system; Photo-electro-Fenton; endocrine disruptor chemical; Toxicity.

5.1. INTRODUCTION

Societal changes, such as fast urbanization and population growth, have made municipal solid waste management an environmental problem [1]. Despite the presence of sanitary landfills and some technological evolutions, such as the control and treatment of gas and leachate production, dumping municipal solid waste into sanitary landfills is not the best solution to the environmental issues, but it is still the most common municipal waste management method in developing countries [2,3].

The most common way to treat sanitary landfill leachate (SLL) is application of a biological oxidation process [4,5]. Since SLL can present different characteristics, older leachate has high ammonium concentrations and non-biodegradable substances due to a methanogenic phase where anaerobic processes takes place in the landfill bed [6–10], maintenance of the microbial communities in technological systems is especially difficult [3]. Since old sanitary landfills ($BOD_5/COD < 0.3$) contain large concentrations of high molecular weight refractory organics, physicochemical techniques have been reported as the better option for their treatment [10–13].

Among physicochemical techniques applied to SLL treatment, Advanced Oxidation Processes (AOPs) [14] and the Electrochemical Process [15] are widely studied showing good results in removing refractory organics compounds. Processes based on Fenton's reaction – where an electron transfer between H_2O_2 and a metal ion (Fe^{2+}) aims to produce hydroxyl radicals ($^{\bullet}OH$) in acid medium [16,17] – are considered especially clean and effective techniques to degrade refractory organic compounds [18]. Among the Electrochemical Advanced Oxidation Processes (EAOPs), electro-Fenton (EF) and photo-electro-Fenton (PEF) processes stand out. Oxidation of the pollutants in EF and PEF occur through an indirect electrochemical oxidation process wherein $^{\bullet}OH$ radicals are produced from Fenton's reaction. This has the advantage as the Fenton reagent (H_2O_2 and Fe^{2+}): is electro-generated *in situ* [19]. These processes may be enhanced with light due to the photolysis of H_2O_2 molecules, which produce extra $^{\bullet}OH$ radicals, and the iron photoactive species, which participates in the removal of the pollutants [18–20]. The high efficiency of the photo-assisted process was recognized in recent studies employing processes derived from Fenton's reaction with light to promote removal of endocrine disruptor chemicals (EDCs) from SLL and reduce toxicity [21,22]. Therefore, photo-electrochemical processes can reach the mineralization removal of refractory organic compounds and inorganic ions [23,24].

Although these processes are related to high removal efficiencies, the permanence of by-products after treatment is still a concern. On the other hand, application of only AOPs is insufficient for wastewater treatment [25,26]. Reis et al. [27] studied a SLL treatment and identified 145 organic compounds in mature landfill leachate, where 70% of the organic compounds were also identified in the raw leachate and 86 compounds were removed by bioreactors systems (conventional bacteria and baker's yeast). However, 19 compounds persisted after the biological treatment steps and were thereby classified by the authors as refractory. Among the persistent compounds found, Bisphenol A (BPA) was identified in treated landfill leachate samples [27,28]. BPA is an industrial chemical, used in polycarbonate plastic and epoxy resin production, causing cellular responses by binding to nuclear estrogen receptors [29]. In a study where environmental risks were assessed by Baderna et al. [28], BPA and 2-ethyl hexanoic acid were reported to be the organic compounds with a higher toxic contribution found in landfill leachates, presenting risks to small rodents and aquatic species.

A recent study by Klauck et al. [30] investigated a SLL treatment by photo-electrooxidation (PEO). After an additional activated carbon (AC) step, (PEO+AC), they measured the presence of organic compounds using GC-MS analyses and found that after the PEO process there was an increase in compounds resulting from the oxidation process. Of those compounds, 28 were identified in raw leachate and 45 were identified after PEO application.

In order to improve pollutant removal and decrease byproduct formation in final treated SLL samples, multistage treatment methods have been studied [11,31–33]. Since SLL has a low biodegradability and conventional treatments are not totally efficient, an alternative method of treatment is needed. Two options are a chemical oxidation process as a pre-treatment aiming to convert initially recalcitrant and non-biodegradable organic compounds into more easily biodegradable intermediates or the application of chemical oxidation process as post-treatment to biological process [4,34–37].

Investigating the performance of an integrated treatment system combining PEF and BO applied to SLL contaminant mineralization is the focus of the current study. The PEF process conditions: current intensity (A), initial concentrations of H_2O_2 (mg·L^{-1}) and Fe^{2+} (mg·L^{-1}) along with electrolysis time (min) were confirmed through a response surface methodology (RSM). The PEF electrolysis time of 0 to 90 min was evaluated sequentially as a function of the color, UV_{254} nm, total carbon (TC), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), BOD_5/COD ratio and concentration decrease. Additionally, the presence of toxic byproducts, recalcitrants, refractory and EDCs were identified by gas chromatography-mass spectrometry (GC-MS). Integrated PEF and BO system strategies were investigated, where the TC initial concentration and the EDC byproducts coming from SLL mineralization were monitored. To confirm the elevated efficiency potential of the integrated system (PEF and BO), toxicity essays with *Artemia salina* were performed and indicated a toxicity reduction from SLL treated samples.

5.2. MATERIAL AND METHODS

5.2.1. Samples, solvents and reactants

Landfill leachate samples were collected from Central Processing Waste, located in the northwestern region of Rio Grande do Sul - Brazil. This wastewater was collected in an equalizer tank and was stored according to Standard Methods [38]. The Sanitary Landfill receives only organic waste, thus it is dumped into sealed cells with gases and wastewater. *Artemia salina* cysts were purchased from Maramarpet. Analytical-grade chemical reagents were used. Deionized water was produced by a Millipore Direct-Ultrapure water system (MilliQ$^{®}$). Sulfuric acid (Vetec, 1.5 M) was used to adjust the pH of the solution. Hydrogen peroxide (ALPHATEC, 35%) and ferrous sulfate heptahydrate ($FeSO_4·7H_2O$, Vetec) were used as Fenton reactants. O_2 from White Martins was added to the solution. For the nutrient solution employed in *Artemia salina* tests as described by Meyer et al. [39] in 1.0 L of Milli-Q water, 23.0 g of NaCl, 11.0 g of $MgCl_2·6H_2O$, 4.0 of Na_2SO_4, 1.3 g of $CaCl_2.2H_2O$ and 0.7 g of KCl were added. A pH of 9.0 was employed and adjusted with Na_2CO_3 (2.5 g·L^{-1}) for the nutrient solution, since this solution was used as negative control for the toxicity tests. BPA was purchased from Sigma Aldrich.

5.2.2. Analytical determinations

H_2O_2 concentrations were evaluated by the metavanadate method described by Nogueira, Oliveira and Paterlini [40]. The color was expressed in Pt-Co units, with a dilution of 1:25. An UV-vis spectrophotometer (Evolution 201/220 – Thermo 168 Scientific) was used as a qualitative measure of the wavelength of simple aromatic compounds (254 nm). A drop in this typical absorbance band related to the well-toxic organic functional group. The solution pH was evaluated and monitored during the reaction time by a pH meter (HANNA, HI 3221). The chemical oxygen demand (COD) was determined by the closed reflux colorimetric method. This methodology was carried out in quintuplicate using a stock solution (Combicheck 20) with 750 ± 75 mg $O_2 \cdot L^{-1}$, obtaining an average result of 742 ± 12.3 mg $O_2 \cdot L^{-1}$. The five-day, biochemical oxygen demand (BOD_5) was measured according to the OECD-301F protocol using an OxiTop (manometric respirometry) system. Total solids (TS), suspended solids (SS), volatile solids (VS) and fixed solids (FS) were determined by a gravimetric method. The analyzes were determined by the procedure described in Standard Methods [38].

The total carbon (TC), inorganic carbon (IC), total nitrogen (TN) and organic carbon (OC) were measured by a TOC analyzer (Shimadzu, TOC-L series), which is based on combustion catalytic oxidation method (680 °C). To estimate the TOC in the centrifuged untreated and treated samples, a detection limit of 4 $\mu g \cdot L^{-1}$ was employed. Conductivity was determined using a conductivity meter (Digimed, DM-32). The total dissolved iron (TDI) concentration was analyzed by total reflection X-ray fluorescence (TXRF) spectrometry (S2 PICOFOX, Bruker AXS Microanalysis GmbH), according to the methodology described by Espinoza-Quiñones et al. [41]. An extraction procedure based on CH_2Cl_2 (3 × 20 mL) was previously performed on 40 mL of treated and untreated landfill leachates samples. After the extraction, the combined organic layer was dried with anhydrous $MgSO_4$ and concentrated by rotary evaporation at 40 ºC. GC-MS analyses were performed employing a GCMS-QP2010 apparatus (SHIMADZU, Japan) equipped with an NST 05 MS column (30 m, 0.25 mm, 0.25 µm coating thickness) composed of dimethyl polysiloxene (95%) and diphenyl (5%). The injector and detector temperature were set at 280 °C, with an interface temperature of 200 °C. For each 1-µL sample, an injection with a split ratio of 1:10 He gas and a flow rate of 1.65 mL min^{-1} was performed. In the equipment, an initial temperature of 50 ºC was set and kept constant for 7 min, with an increase of 25 $ºC·min^{-1}$ until 280 ºC was achieved and held for 20 minutes. The voltage of the GC-MS apparatus was set to 0.88 kV, which provided an electron impact ionization of 70 eV. This facilitated molecular fragmentation and ion production in a mass/electric charge (m/z) field of 25 to 500, which was needed for byproduct concentration determination and structure identification in the samples. The ion source temperature was fixed at 250 ºC in order to select and quantify the organic compounds. A set of organic compounds was comparatively identified based on their characteristic GC-MS patterns using the NIST 08 library available in GCMS-QP2010. The compounds were deemed identified and reported if the similarity percentage was higher than 80%.

Toxicity assays performed with *Artemia salina* followed the methodology described by Meyer et al. [39], employing a so-called Meyer nutrient solution. The cysts were placed in the Meyer solution to hatch in 48 hours and the recipient was divided into a dark and a light side. Larvae from the light side were employed to perform the toxicity tests, in which different SLL dilutions were used and duplicates of 5 mL samples were placed with 10 *Artemia salina* larvae. Meyer solution was used as both a dilution and control solution. After 24 hours, the number of organisms in each tube was measured and the lethal concentration was estimated with a Trimmed Spearman-Karber Method, version 1.5 [42].

5.2.3. Photo-electro-Fenton reactor and experimental procedure

The PEF reactions were carried out in a batch and closed system composed of a box with an inner stainless steel (54 x 42 x 62 cm) coating equipped with magnetic stirrer, glass (1L) and two Hg lamps (Philips 13 W) (λ = 254 nm) as a simulated radiation source UVC. Above the glass, four parallel iron plates (11.9 x 7.0 x 0.2 cm) were used as electrodes (cathode and anode), with a 2.0 cm gap between them and an effective contact area of 155.22 cm^2. The electrodes were arranged in a bipolar way on positive and negative terminals, connected to a power supply (BK precision/1687B, 20 V maximum voltage and 10 A direct current). To support the bipolar connections, two steel bars (2 x 16 cm) were installed as holders, see scheme Figure 1.

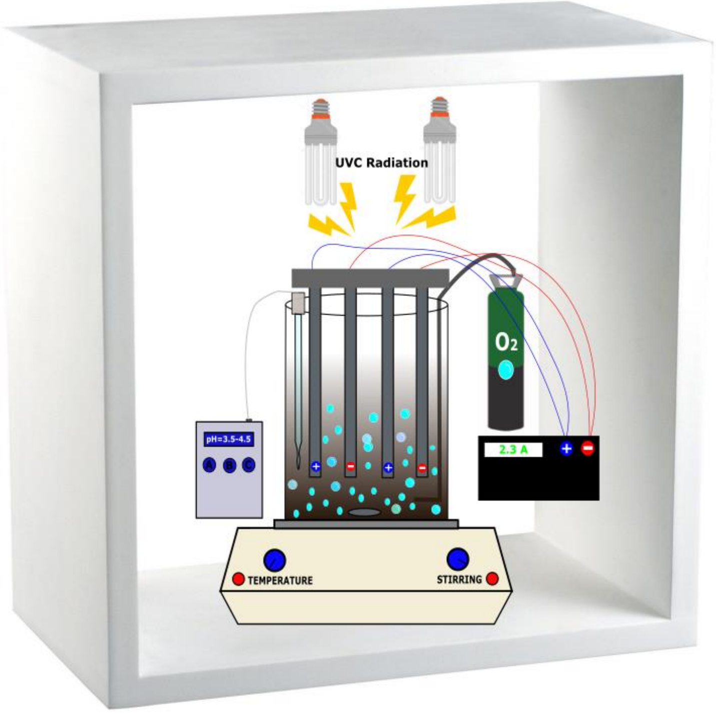


Figure 1. PEF process reactor aparatus.

The experimental runs were based on the addition of 0.8 L of raw SLL in the glass under constant stirring of ~60 rpm. The solution pH was adjusted to the established initial condition and when necessary, the chemical reagents were added. After radiation incidence, dissipation of the steady current intensity and constant O_2 injection of 3.2 L $O_2 \cdot min^{-1}$ were simultaneously triggered for production of the free radicals [43,44]. During electrolysis, a polarity reversal was performed every 15 min to overcome formation of the outer layer. Often, during the electrochemical treatment process, outer layers on the electrodes are formed, which reduces the effectiveness of the technique by increasing the circuit resistance [45].

Preliminary tests with a variation of the main PEF operational parameters were performed. Through the preliminary tests, a RSM was applied which located the best region of the operational conditions providing a high TC degradation efficiency. Performance of the operation conditions determined in the RSM were evaluated as a function of the electrolysis time (0–90 min). During the electrolysis period, the reduction of TC initial concentration, color, absorbance at 254 nm, COD, BOD_5, BOD_5/COD, reaction byproducts as well as the SLL treated samples toxicity took place.

The reduction of treated SLL samples facilitated studying an integration strategy combining the PEF process with biological oxidation, where decreases of the TC initial concentration and reaction byproducts of the applied treatments were also performed.

5.2.4. Biological reactor and procedure

In order to reduce the organic load and toxic substances of the raw SLL, aerated biological oxidation was applied. This system was based on the addition of a mixed consortium of bacteria, fungi, protozoa, organic load and O_2, provided from a dairy company located in the Western State of Parana-Brazil. An activated sludge process was found to be as efficient in partially degrading the organic load from SLL [31,46]. In this work, the biological system of an activated sludge was tested as a pre- or post-treatment strategy for the PEF process. The biological trials were performed in a computer-automated bioreactor (SOLAB, model SL-135) consisting of a 5 L jacketed glass vessel coupled to a thermostatic bath for temperature control.

Initially, 3 L of non-treated or treated SLL was loaded into the bioreactor. The biological runs were conducted under the following conditions: a fixed temperature of 33 ºC, dissolved oxygen near to 3.5 mg $O_2 \cdot L^{-1}$ (50% OD) and a solution pH of 7.0. The samples were taken at 3, 6, 9, 12, 15, 18, 21 and 24 hours of electrolysis time and centrifuged (5000 rpm/10 min) to remove supernatant particles. A sequence of pre-established, physical-chemical, analytical determinations was performed in order to verify the efficiency of the integrated strategy treatment, with biological oxidation as a pre- or post-treatment to the PEF process. Detailed information of the bioreactor (SOLAB, model SL-135), monitoring and measurement probes, stock calibration solutions and experimental condition are described by de Pauli et al. [31].

5.3. RESULTS AND DISCUSSION

5.3.1. Raw SLL and treated samples characterization

Table 1 presents the raw SLL characterization in the PEF treated samples under optimal operation conditions (current intensity of 2.3 A, concentration of 9000 mg $H_2O_2 \cdot L^{-1}$, 60 mg $Fe^{2+} \cdot L^{-1}$ and electrolysis time of 45 min (see Section 3.2)), PEF 45 + Bio 24h, in the PEF optimized conditions (see section 3.2) and biological oxidation (experimental conditions: T= 33 ºC, DO = 3.5 mg $O_2 \cdot L^{-1}$ (DO= 50%), solution pH 7.0, food/microorganism ratio (F/M) of 1, stirring of 500 rpm and aeration of 2 $L \cdot min^{-1}$).

Table 1. Characterization of treated and non-treated SLL samples.

Parameters (units)	**Raw SLL**	**PEF 45 min**	**PEF 45 min. + Bio 24h**
COD (mg O_2 L^{-1})	2441 ± 73	782 ± 47	395 ± 23
BOD_5 (mg O_2 L^{-1})	451 ± 18	315 ± 12	210 ± 8.4
BOD_5/COD	0.18	0.40	0.53
TC (mg C L^{-1})	2225 ± 133	371 ± 17	181 ± 5.4
TS (mg L^{-1})	5000 ± 250	2930 ± 205	1290 ± 64
SS (mg L^{-1})	437 ± 13	322 ± 12	231 ± 14
VS (mg L^{-1})	399 ± 27	194 ± 9	112 ± 4.5
FS (mg L^{-1})	117 ± 6	69 ± 4	54 ± 1.62
TN (mg N L^{-1})	1403 ± 84	846 ± 42	640 ± 32
TDI (mg Fe L^{-1})	11.29 ± 0.45	92.4 ± 5	13.5 ± 0.54
Conductivity (µS cm^{-1})	21.0 ± 1	44.3 ± 1.3	36.3 ± 1
Color (dil. 1:25) (mg Pt-Co L^{-1})	1180 ± 70	89 ± 4.7	88.5 ± 5.3
Turbidity (NTU)	81.0 ± 3	23.6 ± 1.4	36.7 ± 1.5
Absorbance at 254 nm (a.u.)	1.672 ± 0.1	0.18 ± 0.01	0.14 ± 0.01
Solution pH (Sörensen scale)	7.5 ± 0.3	4.3 ± 0.17	7.2 ± 0.3
Temperature (ºC)	23.1 ± 1.4	31.6 ± 1.58	25.4 ± 1.1

Raw SLL had a pH of 7.5, indicating the mature stage of the dumping site [47], which is also denoted by to the low BOD_5/COD ratio. Thus, this SLL had a low biodegradability index [11]. Conductivity values are associated with dissolved inorganic ions in solution, as well as the TDI [48]. The SLL dark color is ascribed to the presence of organic compounds with delocalized pi electrons in conjugated double bonds, called aromatic compounds [49]. The presence of these substances also is confirmed by high absorbance values at 254 nm (UV_{254} nm). The presence of color may affect the photosynthesis process in receptor water bodies, which is also related to solid concentration and the presence of humic substances originating from waste decomposition [50]. These raw SLL characteristics indicate that an advanced electrochemical oxidation process may be a suitable treatment. Such a treatment could reduce recalcitrant organic matter, transforming them into easily biodegradable compounds, thereby facilitating a posterior biological step treatment [10,11,13]. The PEF process increased the biodegradability ratio ($BOD_5/COD = 0.4$) and reduced substances associated with the presence of humic and fulvic acids (254 nm = 0.18 a.u.), which are considered compounds of natural recalcitrance [51]. Excellent performance of the integrated strategy, PEF 45 min + Bio 24 h, was observed in the reduction of parameters such as COD, BOD, TC and TN; reaching residual concentrations of 395 mg $O_2 \cdot L^{-1}$, 210 mg $O_2 \cdot L^{-1}$, 181 mg $C \cdot L^{-1}$ and 640 mg $N \cdot L^{-1}$ respectively. A significant reduction of the initial solid concentrations (TS, SS, VS, and FS) contributed to the raw SLL degradation. The biodegradability ratio ($BOD_5/COD = 0.53$) increase presents the possibility of treated SLL with a satisfactory purification profile for disposal in water bodies in an environmentally clean way.

5.3.2. PEF process preliminary tests

Preliminary tests were performed of the current intensity of 0.5–4.0 A, initial concentration of H_2O_2 of 5000–15000 $mg \cdot L^{-1}$ and Fe^{2+} of 0–100 $mg \cdot L^{-1}$, initial solution pH 3.0–7.0 during electrolysis times of 5 to 90 min (see Fig. 2). The TC initial concentration, pH behavior and residual concentrations of H_2O_2 and Fe^{2+} were also monitored.

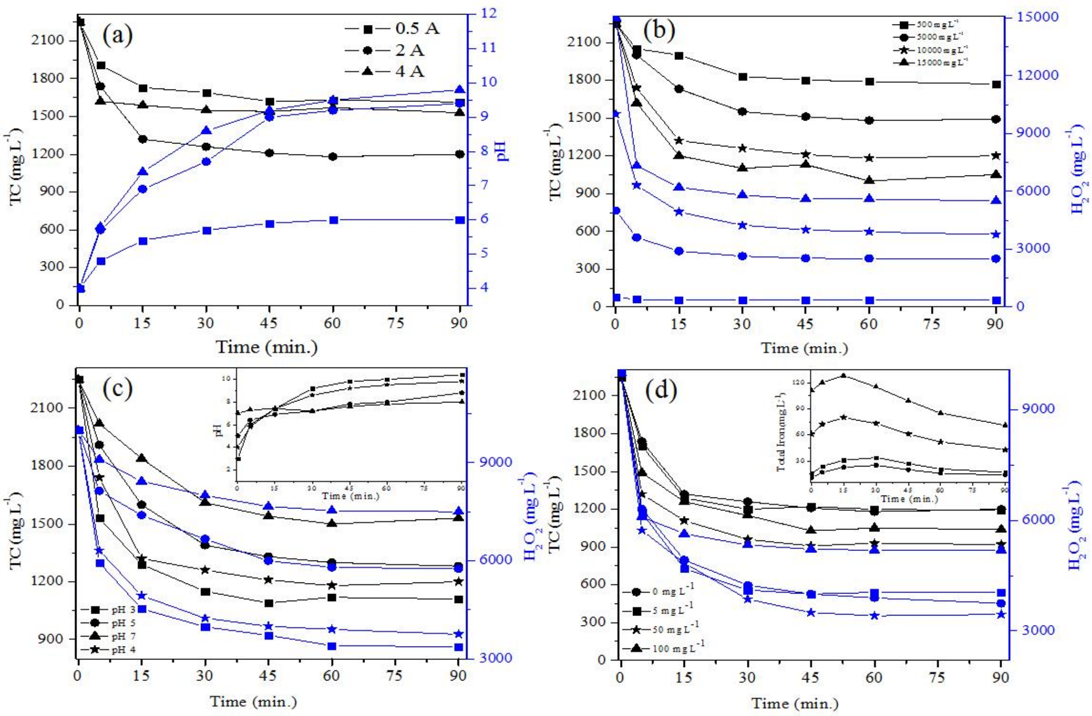


Figure 2. PEF preliminary tests for (a) ΔI, pH 4.0, [H2O2] = 10000 mg·L-1, [Fe2+] = 0 mg·L-1; (b) Δ[H2O2], pH 4.0, I = 2 A, [Fe2+] = 0 mg·L-1; (c) ΔpH, [H2O2] = 10000 mg·L-1, [Fe2+] = 0 mg·L-1, I = 0 A; (d) Δ[Fe2+], pH 4.0, [H2O2] = 10000 mg·L-1, I = 2 A.

Similar behavior for the TC initial concentration was observed between 0.5 and 4 A (see Fig. 3a). However, at 2 A, a higher TC reduction occurred during 15 minutes of electrolysis (≈ 1450 mg·L^{-1}) becoming constant over the course of the reaction since the solution pH increased (> 7.0). The higher pH facilitates side reactions, such as electrocoagulation, where the pollutants are removed by electrostatic attraction and/or complexation reactions [52]. At pH > 6, Fe^{3+} species precipitate as $Fe(OH)_3$ [53] and H_2O_2 decomposes into water and oxygen [44,54,55] resulting in an overall decrease of the desired PEF oxidative reactions.

TC residual concentrations of 1200 and 1050 mg C·L^{-1} were identified in the tested concentrations of 10000 and 15000 mg·L^{-1} of H_2O_2, respectively. A drastic drop of H_2O_2 initial concentration in the reaction medium jumps out at 15 min of electrolysis, remaining constant during the electro-oxidative reaction of PEF process (see Fig 3b). This suggests a process limitation could be ascribed to the increase of solution pH after 15 minutes of electrolysis thereby promoting less oxidative species production such as hydroperoxyl radical ($OOH^\bullet$) and H_2O_2 instability [17,56–58].

A reduction in TC initial concentration was observed ≈ 1300 $mg{\cdot}L^{-1}$ for solutions with pH ranging between 3 and 4 (Fig. 3c), suggesting a high production of hydroxyl radicals in acidic media ($pH \leq 4.5$) [19,59,60].

In Fig. 3d the initial iron concentration (0–100 $mg{\cdot}L^{-1}$) performance is shown: for efficient $^\bullet OH$ production, the ideal iron concentration should be increased. If the dosage is too low there may not be enough iron to produce the required concentration of $^\bullet OH$ radicals necessary for degradation and mineralization of the pollutants. On the other hand, too high of an iron dosage may cause the $^\bullet OH$ radicals to scavenge thru competitive reactions among hydroxyl radicals and ferrous ions [56,57]. Therefore, for an intermediate iron concentration of 50 mg $Fe{\cdot}L^{-1}$ the TC values reached 920 $mg{\cdot}L^{-1}$. In this case, more $^\bullet OH$ radicals were probably produced in the medium as evidenced by the highest H_2O_2 consumption under these conditions.

The preliminary tests of the PEF process variables for the SLL treatment (see Fig. 3) showed two main limiting factors: i) low TC concentration reduction (≈ 1000 $mg{\cdot}L^{-1}$ and/or 53% of the initial fraction) and ii) a constant electro-oxidative reaction when the electrolysis time is greater than 15 minutes. The second limitation suggests that the fast increase in solution pH ($pH > 6$) after 15 minutes leads to H_2O_2 decomposition and less oxidative species production, such as hydroperoxyl radicals ($OOH^\bullet$) [44]. To ensure that the PEF reaction ran over the entire electrolysis time in acid media, the following experiments constantly monitored and adjusted the solution pH to a range of 3.5–4.5.

5.3.3. Response Surface Methodology (RSM)

A RSM evaluation of the PEF process was applied to identify the optimal variable region maximizing the reduction of the TC residual concentration in SLL. A composite central rotational design (CCRD) experiment, carried out over 28 experimental runs (16 factorial points, 8 axial points and 4 replicates at the central points), was applied to probe the main operational parameters of the PEF photoreactor. Investigated parameters included current intensity (q_1) (0–4.6 A), initial H_2O_2 concentration (q_2) (0–18000 mg·L^{-1}), initial Fe^{2+} concentration (q_3) (0–120 mg·L^{-1}) and electrolysis time (q_4) (15–120 min). The results found fluctuations in concentrations of 344 ± 13 to 1404 ± 19 mg·L^{-1}, as is seen in Table 2.

Table 2. CCRD application values.

Run	Current intensity (A)	H_2O_2 (mg L^{-1})	Fe^{2+} (mg L^{-1})	Time (min)	TC (mg L^{-1})		
	Real value **(q_1)**	Real value **(q_2)**	Real value **(q_3)**	Real value **(q_4)**	a	b	c
1	**2.3**	**9000**	**60**	**45**	**346**	**361**	**352**
2	1.1	13500	90	30	1050	1039	1098
3	1.1	4500	90	60	1290	1281	1200
4	2.3	9000	120	45	515	509	503
5	2.3	9000	0	45	890	894	903
6	2.3	9000	60	15	590	579	607
7	1.1	13500	30	60	890	898	881
8	3.4	13500	90	60	710	704	721
9	2.3	9000	60	75	410	407	396
10	3.4	4500	30	30	820	821	812
11	2.3	18000	60	45	840	837	845
12	1.1	4500	90	30	1410	1400	1405
13	1.1	13500	30	30	970	972	976
14	4.6	9000	60	45	730	733	721
15	**2.3**	**9000**	**60**	**45**	**353**	**351**	**347**
16	3.4	13500	30	30	840	849	831
17	1.1	4500	30	30	1385	1378	1327
18	1.1	13500	90	60	990	1001	981
19	0	9000	60	45	1100	1110	1081
20	3.4	13500	90	30	680	699	662
21	3.4	4500	30	60	850	862	831
22	1.1	4500	30	60	1400	1425	1388
23	3.4	13500	30	60	590	581	579
24	3.4	4500	90	30	914	900	910
25	3.4	4500	90	60	934	899	921
26	2.3	0	60	45	1350	1365	1366
27	**2.3**	**9000**	**60**	**45**	**351**	**342**	**348**
28	**2.3**	**9000**	**60**	**45**	**340**	**333**	**359**

A polynomial model was used to adjust the coefficients q_1, q_2, q_3, and q_4 (see Eq. 1). Unitary or simultaneous-interaction, linear and quadratic fits of the experimental data (standard deviation of ≈ 5%) showed a TC concentration reduction of 320 mg·L^{-1} (see by Eq. 2) close to the real TC concentration (344 ± 13 mg·L^{-1}) observed in experimental runs 1, 15, 27 and 28 (CCRD central point).

$$R = a_0 + \sum_{i=1}^{k} a_i q_i + \sum_{i=1}^{k} a_{ii} {q_i}^2 \sum_{i} \sum_{i<j} \sum_{j} a_{ij} q_i q_j \tag{1}$$

In the preceding equation, R is the response variable, q_i and q_j are independent variables, a_0 is the intercept term, a_i is a coefficient determining the influence of parameter i in the response (linear term) and a_{ij} refers to the interaction effect.

$$R_{[TC]} = 3895.2 - 839.2*q_{1(L)} + 130.2*q_{1(Q)} - 17.7*q_{3(L)} + 0.13*q_{3(Q)} + 0.01*q_{2(L)}*q_{1(L)} + 0.03*q_{1(L)}*q_{3(L)} + 0.26*q_{4(L)}*q_{1(L)} + 0.00002*q_{2(L)}*q_{3(L)} + 0.02*q4_{(L)}*q_{3(L)} - 2043 \tag{2}$$

The *F-test* analysis (*two-way* ANOVA - $p < 0.05$, data not shown) validated the polynomial model (Eq. 1 and 2) with determined values of F_{calc} (43) > F_{tab} (1.43). The good experimental data fit, predicted as a function of the observed values, is shown in Supplementary Material Fig. 1SMa. Significant effects ($p > 0.05$) were observed in the unitary coefficients, $q_{2(Q)}$, $q_{1(Q)}$, $q_{1(L)}$, $q_{2(L)}$, $q_{3(Q)}$, $q_{4(Q)}$ and $q_{4(L)}$, along with the simultaneous interaction of $q_{1(L)*}q_{2(L)}$ highlight the importance of the TC residual concentration in SLL, as is shown by the Pareto analysis in Supplementary Material (see Fig 1SMb).

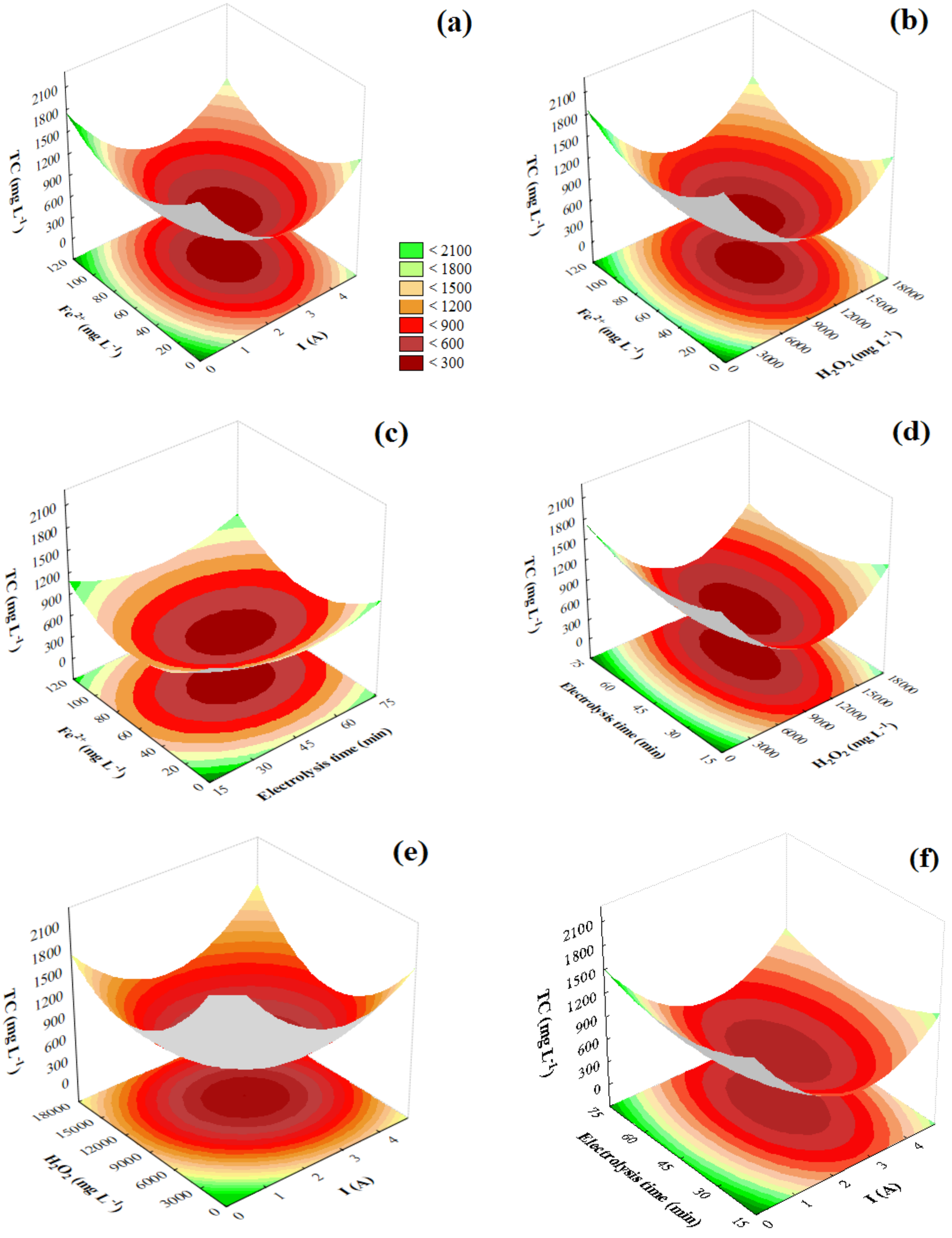


Figure 3. The 3-D surface used for interpreting TC concentration reductions in SLL. Experimental conditions were fixed at: I = 2.3 A, [H2O2 = 9000 mg· L-1], [Fe2+ = 60 mg·L-1] and an electrolysis time of 45 minutes.

In Fig. 3, the performance of the PEF process variables is presented in the 3-D surface as a function of the TC concentration reduction from SLL, which was investigated in the CCRD. For Fe^{2+} concentrations of 0–40 $mg{\cdot}L^{-1}$ and 80–120 $mg{\cdot}L^{-1}$ a low TC concentration reduction was seen as a function of the current intensity (A) (see Fig 3a), H_2O_2 concentrations (see Fig 3b) and electrolysis time (min) (see Fig 3c). The undesired increase in Fe^{2+} concentration during the electro-oxidative reactions may afford adverse effects, such as competitive reactions among hydroxyl radicals and ferrous ions, scavenging $^{\bullet}OH$ radicals [56,57], which leads to a limitation in the pollutants found in SLL removal. A better performance in the PEF process was observed with H_2O_2 concentration range of 9000–11000 $mg{\cdot}L^{-1}$ as a function of the electrolysis time of 40–60 minutes (see Fig. 3d) and current intensity of 2–3 A (see Fig. 3e). The excess H_2O_2 in the reactive medium provides a large hydroxyl radical ($^{\bullet}OH$) sink leading to structures such as hydroperoxyl radicals ($OOH^{\bullet}$). These species are more selective and less oxidative than $^{\bullet}OH$, thereby minimizing the PEF process efficiency in decreasing the TC concentration in the SLL. Fig 3f confirms the best performance of the PEF process in the operational conditions with a current intensity of 2.3 A, H_2O_2 concentration of 9000 $mg{\cdot}L^{-1}$, Fe^{2+} concentration of 60 $mg{\cdot}L^{-1}$ and an electrolysis time of 45 minutes; reaching a minimum TC residual concentration of 344 $mg{\cdot}L^{-1}$ in the SLL.

5.3.4. Study of color, UV_{254} nm, TC, COD and BOD_5 removal

To determine the optimal conditions of the reactor's dependent parameters, an RSM analysis based on a CCRD was applied (see section 3.3). The optimal conditions were found to be 9000 mg H_2O_2 L^{-1}, 60 mg $Fe^{2+}{\cdot}L^{-1}$, I = 2.3 A and a solution pH range of 3.5–4.5. Fig. 4 presents the color, UV_{254} nm, TC, COD and BOD_5 removal results, as well as the BOD_5/COD ratio increase at these conditions with different electrolysis times (0–90 minutes).

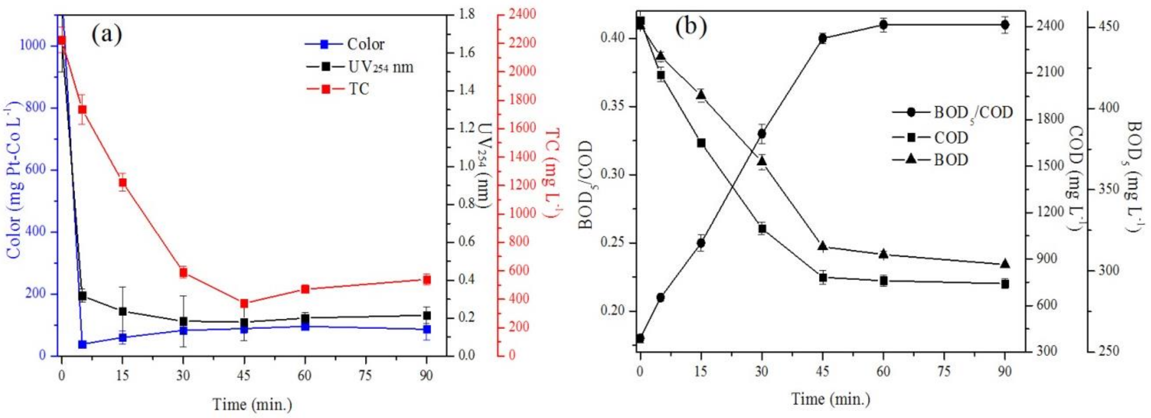


Figure 4. (a) Color, UV254 nm and TC removal (b) COD removal, BOD5 removal and BOD5/COD ratio increase at operating conditions of 9000 mg H2O2·L-1; 60 mg Fe2+·L-1; I = 2.3 A and a solution pH range: 3.5–4.5 in electrolysis times of 0–90 minutes.

According to Dia et al., [49] absorbance at 254 nm is measured to estimate the degree of aromaticity for different organic fractions in landfill leachates. These leachates are mainly characterized by the presence of humic (HA) and fulvic acids (FA) since they present alkyl-aromatic units linked mainly by oxygen and nitrogen groups such as carboxylic acid, phenolic and alcoholic hydroxyls, ketone and quinone groups [61,62]. A process involving oxidative reactions such as the Fenton reaction and its derivation are capable of removing high molecular weight organics like HA preferentially [63–65]. In Fig. 4a the organic fraction related to HA, measured through the UV_{254} nm, was removed faster than the FA fraction.

Dia et al. [49] suggest that HA molecules contain more aromatic rings than FA, because HA presented 62% of the total 254 nm absorbance, although FA had a higher TOC value (TOC_{FA} 102 mg C/L versus TOC_{HA} 85 mg C/L). As FA presented higher TOC values than HA, once the fulvic fraction is removed, the TC values decrease slower than 254 nm absorbance ones. The color removal is associated with a reduction in the 254 nm absorbance since HA confer color to SLL [49].

As a result of these operational conditions, the electrolysis time providing the best removal rates was 45 minutes, reaching 89 mg Pt-Co·L^{-1} of color, 254 nm = 0.18 a.u., 370 mg·L^{-1} of TC, 315 mg·L^{-1} BOD_5, 782 mg·L^{-1} COD and improving the ratio BOD_5/COD = 0.4 (Fig 4b).

After 45 minutes, constant values of BOD_5 and COD along with a tendency to increase the TC value were observed; this fact may be a result of the formation of chemical oxidation byproducts. As reported by Ramírez-Sosa et al., [66] $^{\bullet}OH$ radicals cause changes in the structure of organic compounds; oxidizing recalcitrant organic substances present in the landfill leachate. As observed by Klauck et al., [67] the oxidation of HA and FA were mainly responsible for the generation and increase of carboxylic acids, alkanes, ketones and alcohols in samples treated by the advanced oxidation process. This increased the organic compounds identified by GC-MS after the applied process.

The EAOPs are efficient processes for removing persistent pollutants as well as for increasing the biodegradability of SLL [30,67]. However, the oxidation of complex organic compounds may have consequences, such as byproducts production, evidencing the importance of studying this production process and the remaining byproducts, which can be more toxic than parent compounds [68]. Samples of (a) raw SLL and SLL samples after treatment with the PEF process for different electrolysis times: (b) 5 minutes, (c) 15 minutes, (d) 30 minutes, (e) 45 minutes were collected and analyzed by GC-MS. The resulting chromatograms indicating the organic compounds present in each sample are shown in Fig. 5.

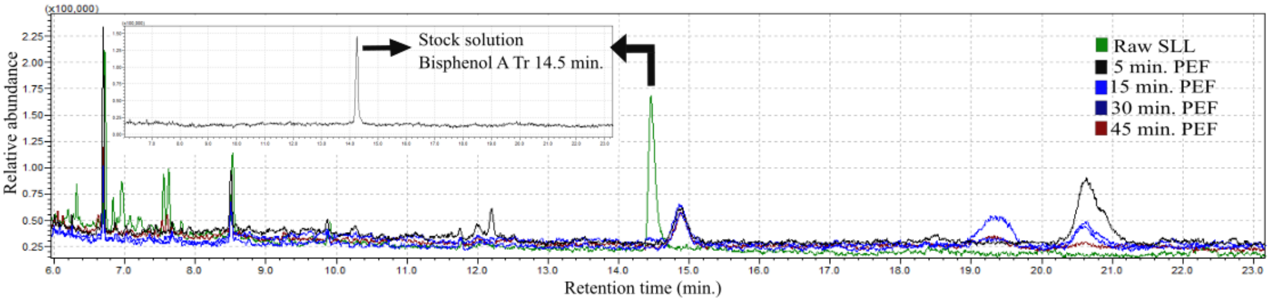


Figure 5. GC-MS chromatograms of (a) raw SLL (green) and SLL samples treated by the PEF process after (b) 5 minutes (black), (c) after 15 minutes (light blue), (d) after 30 minutes (dark blue) and (e) after 45 minutes (brown).

In Fig. 5, the raw SLL sample contained: N,N-diethyl-3-methylbenzamide*, triallyl isocyanurate*, O-toluene ethyl sulfonamide*, cyclohexane,1,1,3-trimethyl-2-(3methylpentyl), 1-3-cyclohexanedione,2,4,6-trimethyl, diisobutyl phthalate*, dipentyl phthalate* and BPA* (Tr = 6.3, 6.7, 6.8, 7.55, 7.62, 8.5, 9.9 and 14.5

minutes, respectively). Compounds denoted with an * are listed by the EPA as endocrine disruptor chemicals [69].

Phthalic acid esters (PAEs) and BPA are usually found in landfill leachates [27,70–72]. Jeong et al. [73] evaluated the reproductive and toxicological effects of BPA on an aquatic ecosystem employing *Daphina Magna* and identified significant genetic variations in the studied biomarkers. Therefore due its high toxicity and abundance in SLL, BPA concentration was confirmed by a stock solution (See Fig. 5 in details).

During the oxidative process some compounds were formed; after 5 minutes of the PEF process: octathiocane (Tr = 12.2 min), mono(2-ethylhexyl) phthalate (Tr = 14.9 min) and bis(2-ethylhexyl) terephthalate* (Tr = 20.6 min), after 15 minutes of the PEF process: diisodecyl phthalate (Tr = 19.38 min) and after 30 minutes of the PEF process: diisooctyl phthalate (Tr = 14.9 min). After 45 minutes of electrolysis, a significant organic fraction was degraded but certain persistent compounds remained: triallyl isocyanurate (TAIC) (Tr = 6.7 min), diisobutyl phthalate (DiBP) (Tr = 8.5 min) and diisooctyl phthalate (DIOP) (Tr = 14.9 min) (Fig. 5). The persistence of these compounds can be attributed to their sorption on the dissolved organic matter, especially during the oxidation step. A low solution pH leaves the functional groups of dissolved organic matter undissociated and keeps them suspended in solution. This facilitates opportunities for the EDCs to adsorb onto the dissolved organic matter [74–76].

TAIC is a multi-functional olefin monomer used as crosslinking agents for biodegradable polymers to improve thermal and mechanical properties [77]. Rong and Sun [78] studied TAIC degradation by AOPs and identified competition between the TAIC molecule and the decomposition of the intermediate products. Due to this, the active radicals concentration were not high enough to oxidize all the intermediates and TAIC molecules. Therefore, persistence of TAIC in PEF treated samples may be due to the competition between intermediates products and TAIC molecules since the treatment time or the generated oxidative radicals could not degrade TAIC.

Phthalate esters are used as plasticizers to provide flexibility and resilience to plastic products. These compounds are not covalently bound in the products that they are used, thus it can leach into the environment [79]. As reported by Borch et al., [80] DiBP causes adverse effects on the developing male reproductive system. DiBP is used as Di-n-butyl phthalate (DnBP) substitute. Both are banned in toys and child-care products in the EUA and Europe along with in cosmetics due to their classification as reproductive toxicants [81]. DiBP persisted for the whole oxidative treatment, which is in agreement with other studies. DiBP was found in SLL samples after a treatment performed using PEO+AC as described by Klauck et al. [67]. A small part of this compound remained in SLL after a Fenton process reported by He et al. [75].

DIOP is a phthalic acid diester employed as plasticizer for synthetic rubber and vinyl, cellulosic and acrylate resins [82]. Saillenfait et al. [83] showed that DIOP disrupted the male rat sexual differentiation by the same mechanism of action as the antiandrogenic C4-C6 phthalates. It caused the same pattern of male reproductive effects, although it was less potent than DiBP, Dibutyl phthalate (DBP), DnHP, and Di(2-ethylhexyl) phthalate (DEHP) in inducing male reproductive tract malformations.

The presence of persistent pollutants in the environment is raising concerns about their toxicological effects on living organisms, especially since they cannot be totally removed by conventional SLL treatments [84]. Application of techniques promoting the degradation or mineralization of these compounds, such as two-stage integrated system photo-electro-Fenton and biological oxidation process, is therefore warranted.

5.3.5. Integrated systems – PEF process and biological treatment

Electrochemical oxidation processes have been reported as effective treatments for the removal of endocrine disruptors like BPA and aniline [85]. Nevertheless, Mandal, Dubey and Gupta [24] identified that the electrochemical oxidation process may be not adequate to be applied alone. Therefore, is it important to study sustainable process in tandem with efficient technologies. The so called Bio-EF process - a combination of electrochemical and biological treatments – is supposed to couple the advantages of both process and can be performed with EF as either a pre or post-treatment. The treatment sequence depends on the type and characteristics of the wastewater [86].

To evaluate the performance of the integrated system and its optimium configuration, TC profiles are presented in Fig. 6. The profiles are from three methods: after 45 minutes of electrolysis PEF process was integrated with BO at different times (3, 6, 9, 15, 18, 21 and 24 h) (PEF 45 min + 24 Bio), only BO after different times (Bio 24 h) and BO at times: 3, 6, 9, 15, 18, 21 and 24 h were integrated with 45 minutes of PEF process (Bio 24 h + PEF 45 min).

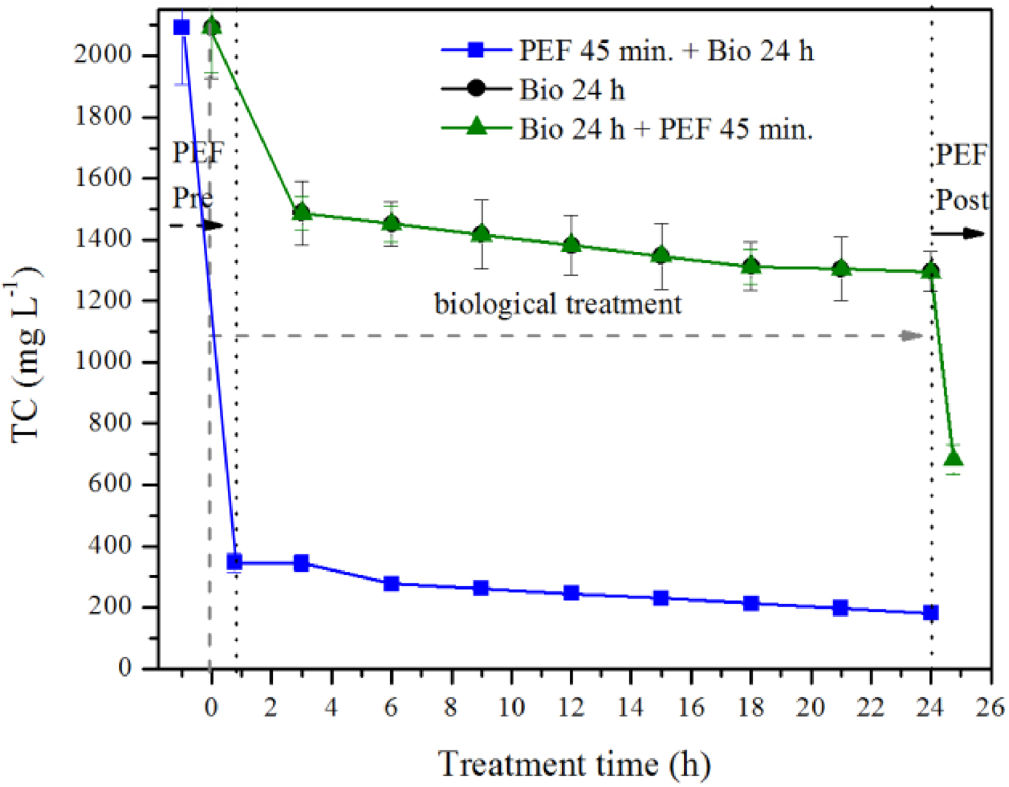


Figure 6. TC removal profiles for the PEF process after 45 minutes of electrolysis integrated with BO (PEF 45 min + 24 Bio h); only BO (Bio 24 h) and BO at times: 3, 6, 9, 15, 18, 21 and 24 h integrated with 45 minutes of PEF process (Bio 24 h + PEF 45 min).

The SLL treated after 24 hours of the process lead to a 38% reduction (1380 mg·L^{-1}) of TC (see Fig. 6). As reported by Baiju et al., [11] high BOD_5/COD ratios and low-molecular, organic weight concentrations identify a young SLL ($BOD_5/COD > 0.6$) that is susceptible to treatment by biological processes. Nevertheless, this SLL presented a $BOD_5/COD = 0.18$ and thus it was categorized as a mature SLL ($BOD_5/COD < 0.3$). Therefore, physicochemical techniques is a better option for its treatment [11]. Furthermore, toxic substances such as polyaromatic hydrocarbons, adsorbable organic halogens, and polychlorinated biphenyls may create an inhibitory effect and reduce the microbial system efficiency [87].

Electrolysis time of 45 minutes in the PEF process were able to reduce 371 mg·L^{-1} from the residual 181 mg·L^{-1} of TC concentration on the integrated system with posterior BO (see Fig. 6). According to Baiju et al., [11] in the combined process, EF as a pre-treatment can transform persistent organic pollutants into more biodegradable intermediates, thus the biological process can easily remove them. Whereas, electro-coagulation also occurs in the PEF process, the improvement in TC removal with the integrated system in comparison to biological treatment as a single step also can be explained by the hydrolysis of some macromolecules, as shown by Djelal, Lievre and Ricordel [88].

When a biological step was applied as a pre-treatment, the initial TC concentration removal rate was lower. This may be due to the high presence of recalcitrant compounds and compounds of difficult biodegradation. Even with the PEF process applied as a posterior treatment step, the total TC removal achieved 68% (712 mg·L^{-1}) (see Fig. 6). This is understood by the presence of suspended microbial cultures in the SLL treated with a post-biological step. As a result, some of the hydroxyl radicals produced during PEF attack the outer membrane of the bacteria acting as an $^{\bullet}$OH scavenger, which reduce the TC removal rates [86,89,90].

Therefore the most suitable configuration of the two-stage treatment was PEF 45 min + Bio 24 h. This is in agreement with the Comniellis et al. [91] treatment strategy where not biodegradable wastewater is treated by an advanced technique before biological post-treatment.

In order to evaluate the byproducts formation, GC-MS analyses were performed with the same integrated systems described above, and their results are shown in Fig. 7.

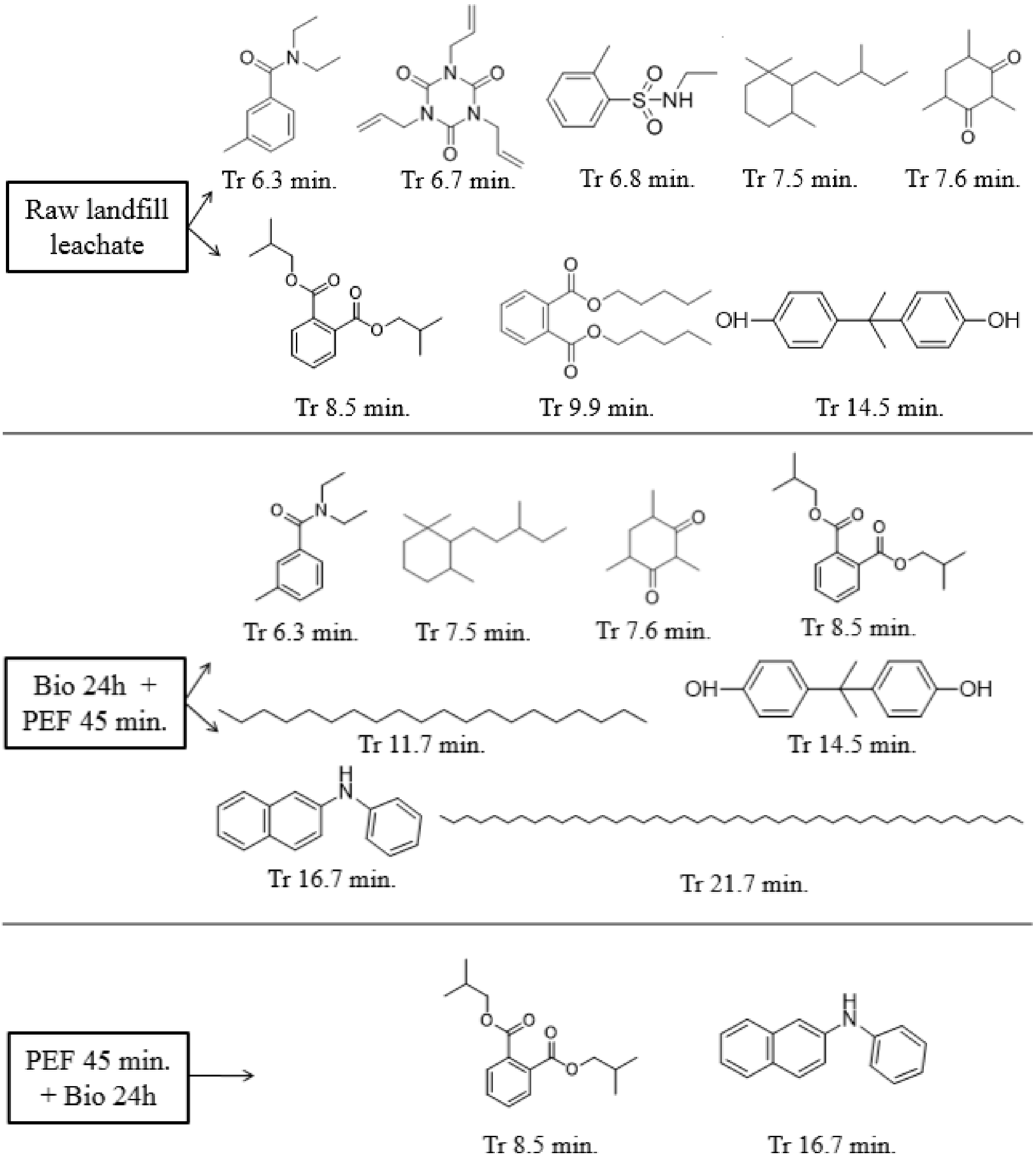


Figure 7. GC-MS analysis of byproduct formation in raw SLL organic products analysis and applied integrated system treatments (Bio 24h + PEF 45 minutes and PEF 45 minutes + Bio 24 h).

BO as a pre-treatment step was not able to remove BPA (Tr = 14.5 min) from the treated SLL samples apart from the generation of two byproducts: eicosane (Tr = 11.7 min) and tetratetracontane (Tr = 21.7 min).

Another concern is the sorption of pollutants onto the surface of bacterial cells and/or dissolved organic matter. If this is not properly treated, it will be disposed with the sludge and depending on further sludge treatment can contaminate the hydrosphere and soils [92–94]. Maybe some pollutants from the raw SLL could be absorbed into the dissolved organic matter and/or the bacterial cells and were difficult to degrade in the biological step. Thus in the applied PEF process, the presence of microbial cultures acted as an $^{\bullet}$OH scavenger reducing its removal efficiency on adsorbed pollutants. As presented on Fig. 7, Bio 24 h + PEF 45 min showed more organic compounds compared to PEF 45 min + Bio 24 h. In the second treatment mode, $^{\bullet}$OH could better attack organic compounds making them more biodegradable and/or degrading them. The biodegradability enhancement is related to the reduction of toxicity [95], as show in Table 3. The PEF 45 min + Bio 24 h presented the lower toxicity of the all the treatment strategies tested in this work.

The electrochemical oxidation is related to high-level organic compound transformation into low-molecular weight organic compounds [24]. Thus its detection by GC-MS may be difficult, as can be noted by the low number of compounds identified in the PEF 45 min + Bio 24 h system. On the other hand, Gazenko et al. [86] reported that a biological process to treat pharmaceutical wastewater was more efficient after the EF process because of the higher biodegradability enhancement.

5.3.6. Toxicity assays

Toxicity assays employing *Artemia salina* were performed. The mortality in six different dilutions of raw and treated SLL samples (the standalone PEF process, the standalone BO process, the PEF 45 min + Bio 24 h integrated system and the Bio 24 h + PEF 45 min integrated system) are reported in Table 3.

Table 3. Mortality fractions of 20 Artemia salina populations exposed to six different dilutions of raw SLL and samples treated by the PEF process, the biological process and as a combined strategy.

Samples	**Mortality on six different dilutions of raw SLL and SLL treated samples after standalone PEF and BO and as integrated systems**	**LC_{50} (%)**	**Confidence interval**

	1%	3%	10%	30%	50%	100%		
Raw LL	07/20	08/20	08/20	20/20	20/20	20/20	7.00	2.82-28.94
Bio 24h	04/20	04/20	02/20	10/20	20/20	20/20	17.00	16.84-29.52
PEF 45 min.	04/20	04/20	02/20	10/20	20/20	20/20	20.00	16.37-37.64
PEF 45 min. + Bio 24h	02/20	02/20	04/20	04/20	20/20	20/20	33.00	28.94-40.77
Bio 24h + PEF 45min.	04/20	03/20	00/20	20/20	20/20	20/20	26.00	22.50-37.66

Artemia salina is commonly used to evaluate the toxicity of wastewaters in SLL since this organism lives in salt lakes and tolerates high salts concentrations similar to those found in landfill leachates [96].

Dilutions above 50% of both raw and treated SLL samples were responsible for 100% of tested organism mortality. However, a greater TC removal (see Fig. 4), smaller intensity and disappearance of toxic compounds detected by GC-MS (see Fig. 7) was observed for the process PEF 45 min + Bio 24 h, due to the lower medium toxicity of this system: LC_{50} of 33%.

Generally, biological processes as a pre-treatment aim to reduce wastewater organic load as well as increase electrochemical oxidation. As a post-treatment, these processes aim to remove remaining and recalcitrant organic species [24]. Nevertheless, in this work the system in which biological oxidation was used as pre-treatment step did not present the best results. Among the compounds confering toxicity to the landfill leachate are EDCs [67] and they can be sorbed on the dissolved organic matter in leachate [75]. Therefore, as far as the biodegradable organic load is degraded during the biological step, EDCs are released in solution, which may confer toxicity to the samples even after the treatment. Whereas EDCs need a strong oxidative attack for degradation, such as that performed by $^{\bullet}$OH, the PEF process is better suited to transform molecules that are recalcitrant in the biological step, The more biodegradable products resulting from the PES process are easily degraded with the biological step as a post-treatment.

Klauck et al. [30] studied different treatments for landfill leachate and reported that PEO was the most favorable AOP for toxicity reduction. The same authors infer that an integrated system of photo-electrochemical oxidation, electrochemical oxidation and ozonation at an alkaline pH lead to changes in the landfill leachate matrix. Byproducts were probably still generated, but with lower toxicity than compounds present in raw landfill leachate. This agrees with the results found in this study. The reaction byproducts were generated, however, the SLL organic load was reduced as well as its toxicity. The best system configuration was pre-treatment with a PEF process and post-treatment with a biological.

5.4. CONCLUSION

Emerging pollutants found in SLL are increasing the concern about its effects in the human body and aquatic ecosystems. Among these pollutants, potential EDCs were identified in the present work. An SLL treatment was investigated by applying a PEF process as a unitary treatment strategy; with the application of a CCRD to determinate the PEF suitable operating conditions and byproducts analysis performed by GC-MS. It was found that after 45 minutes of electrolysis, organic pollutants intensity was reduced as well as byproducts formation. It is worth noting that BPA was found in raw SLL samples and after the proposed PEF treatment it was degraded. With the photo-electro reactor operating with 9000 mg $H_2O_2{\cdot}L^{-1}$, 60 mg $Fe^{2+}{\cdot}L^{-1}$, I = 2.3 A, solution pH range: 3.5–4.5 and O_2 injection, the SLL treated samples presented 89 mg $\text{Pt-Co}{\cdot}L^{-1}$ of color, 254 nm = 0.18 a.u., 370 $mg{\cdot}L^{-1}$ of TC, 315 $mg{\cdot}L^{-1}$ BOD_5, 782 $mg{\cdot}L^{-1}$ COD, and BOD_5/COD = 0.4. Therefore at these operational conditions, a combination of the PEF process and biological treatment was investigated. Thus, it was studied if the PEF process was more suitable for application as pre-treatment to a further BO step or as post-treatment to a BO step. The PEF process applied as pre-treatment provided the best results, due to transformation of the organic refractory compounds into more biodegradable compounds, susceptible for treatment by a biological system. The byproducts formation was also performed for the integrated systems, where, the PEF 45 min + Bio 24 h integrated process showed the lowest byproducts amount This improved the toxicity of the SLL treated samples by presenting a CL_{50} of 33% for this integrated system strategy.

Acknowledgments

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5.6. SUPPLEMENTARY MATERIAL

5.6.1. LIST OF SUPPLEMENTARY FIGURES

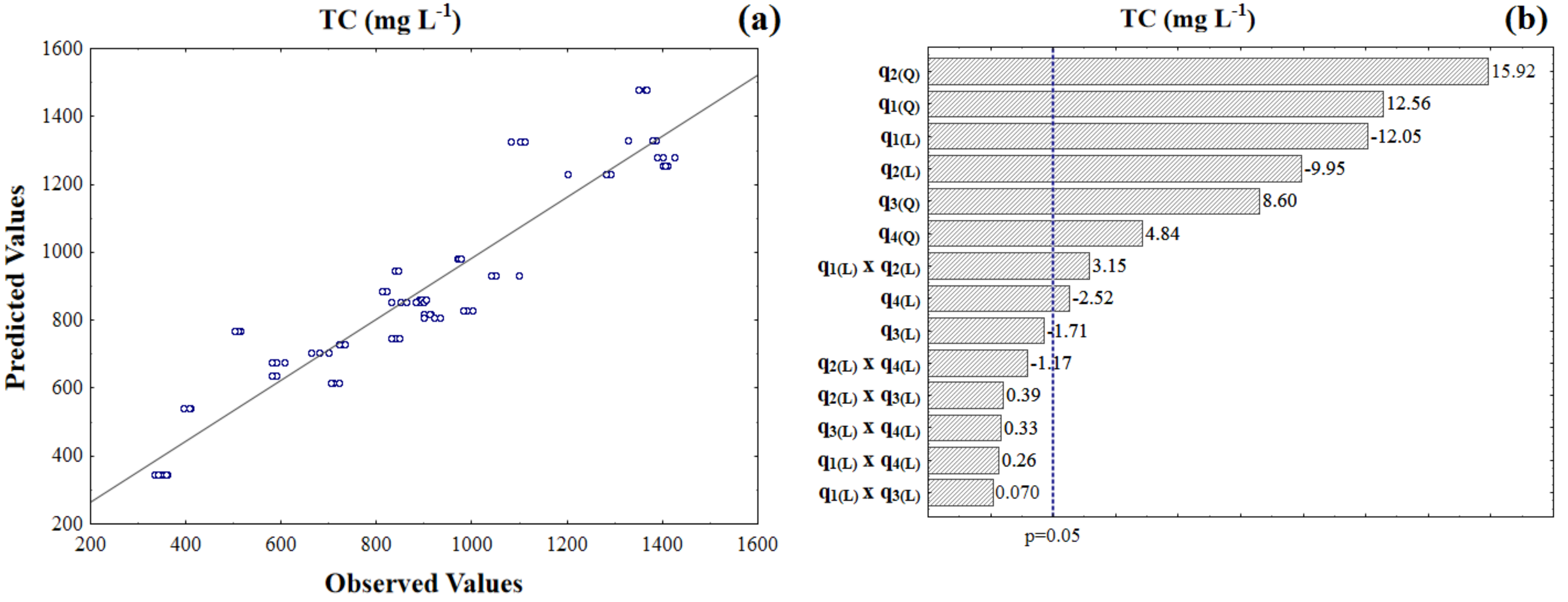

Figure SM 1. The graph obtained by the CCRD application for the TC concentration reduction (mg L-1) a) Predicted values by observed values b) Pareto's analysis of (q1, q2, q3, and q4) variables in linear (L) and quadratic (Q) terms.

[redacted] 6. CONCLUSÕES GERAIS

Contaminantes emergentes encontrados em LAS estão aumentando a preocupação sobre seus efeitos em humanos e ecossistemas aquáticos. De acordo com a revisão bibliográfica realizada, BPA, PAEs; surfactantes: BPA, DBP, DEHP, DEP, NP, BBP, DOP, DMP, 4OP, DiBP, DTBP e nicotina foram os EDCs mais frequentemente encontrados em LAS em diferentes países, incluindo a detecção de alguns destes no LAS empregado no presente estudo. Dentre estes contaminantes, além de elevados teores orgânicos, EDCs foram identificados no LAS estudado. O tratamento do LAS foi investigado primeiramente através da aplicação do processo FEF de forma unitária onde experimentos preliminares e uma MSR foram empregados para determinar as condições operacionais ótimas do foto-reator, operando com eletrodos de ferro fundido, sendo estas: 9000 mg H_2O_2 L^{-1}; 60 mg Fe L^{-1}; I=2,3 A; pH entre: 3,5-4,5 e injeção de O_2 a taxa de 3,2 L O_2 min^{-1}. Para estas condições, os subprodutos gerados durante a foto-eletro-oxidação foram identificados através de análises de CG-MS, bem como foi realizado o estudo das condições de toxicidade das amostras brutas e tratadas, concluindo-se que após o processo foto-eletro-químico, a toxicidade das amostras diminuiu, com isto, possibilitou-se o estudo da integração do processo FEF com uma etapa de tratamento biológico, onde a melhor estratégia de tratamento também foi investigada.

Neste estudo, o processo FEF seguido de etapa de tratamento biológico apresentou as melhores condições de diminuição da toxicidade e maiores taxas de remoção dos compostos estudados, o que foi relacionado à transformação de compostos orgânicos refratários em compostos mais biodegradáveis, susceptíveis a serem tratados por um posterior processo de oxidação biológica. No caso da aplicação do tratamento biológico seguido da foto-eletro-oxidação, supõe-se que as condições iniciais do LAS bruto não eram adequadas para a aplicação de processos biológicos (DBO_5/DQO=0,18) e a presença de culturas microbianas resultantes do prévio tratamento biológico, possivelmente atuaram como sequestradores de $^{\bullet}OH$ no processo FEF subsequente, fazendo com que as remoções deste processo fossem menores. Os subprodutos gerados após as etapas de integração de sistemas e a toxicidade das amostras também foram estudados, concluindo-se que o processo FEF 45 min. + Bio 24 h apresentou a menor geração de subprodutos e as melhores condições de redução da toxicidade do LAS tratado, apresentando uma CL_{50} de 33%.

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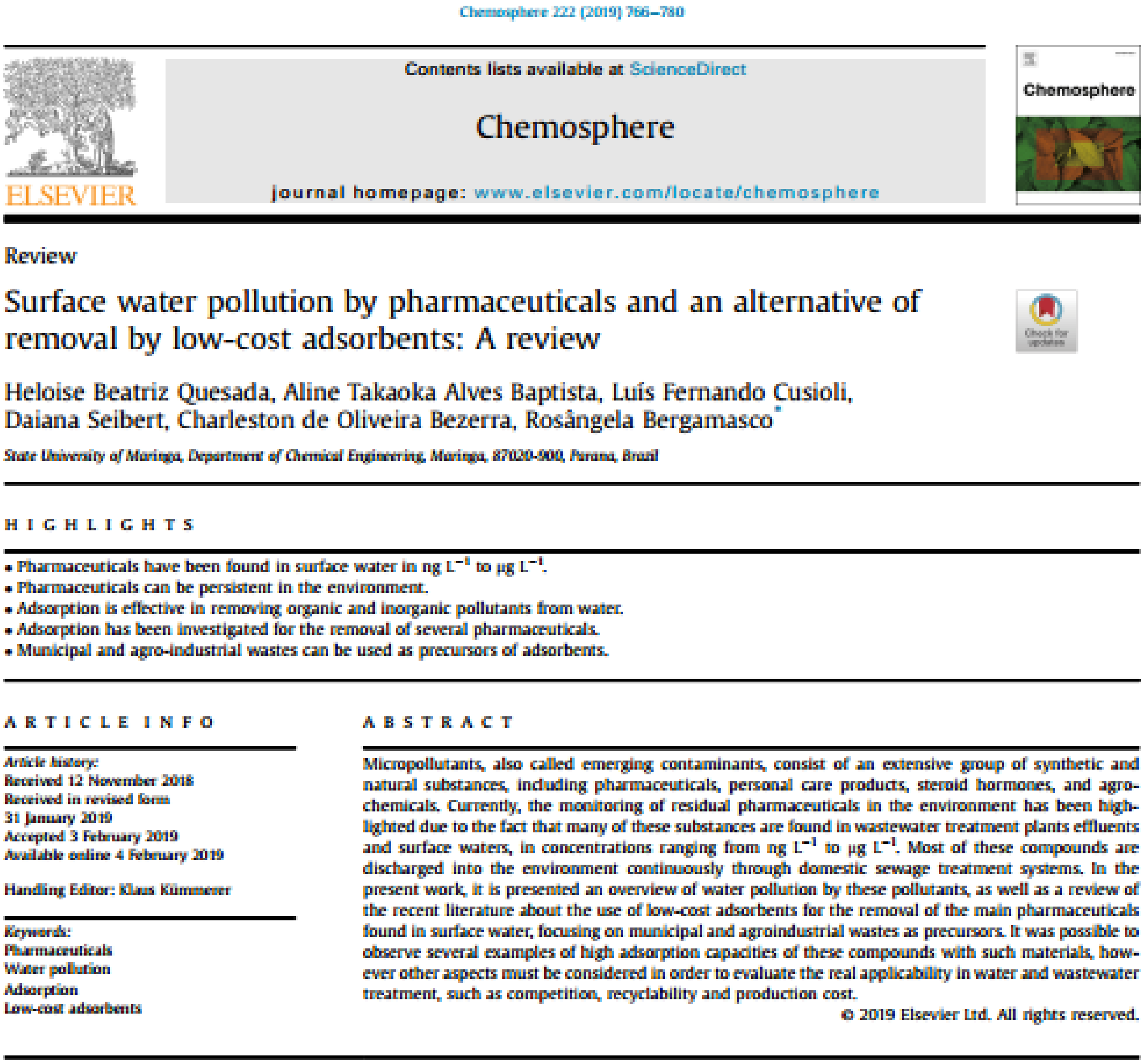
APÊNDICE A – ARTIGOS PUBLICADOS EM COLABORAÇÃO

Artigo 1



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Review

Surface water pollution by pharmaceuticals and an alternative of removal by low-cost adsorbents: A review

Heloise Beatriz Quesada, Aline Takaoka Alves Baptista, Luís Fernando Cusioli,
Daiana Seibert, Charleston de Oliveira Bezerra, Rosângela Bergamasco*

State University of Maringa, Department of Chemical Engineering, Maringa, 87020-900, Parana, Brazil

HIGHLIGHTS

- Pharmaceuticals have been found in surface water in ng L^{-1} to μg L^{-1}.
- Pharmaceuticals can be persistent in the environment.
- Adsorption is effective in removing organic and inorganic pollutants from water.
- Adsorption has been investigated for the removal of several pharmaceuticals.
- Municipal and agro-industrial wastes can be used as precursors of adsorbents.

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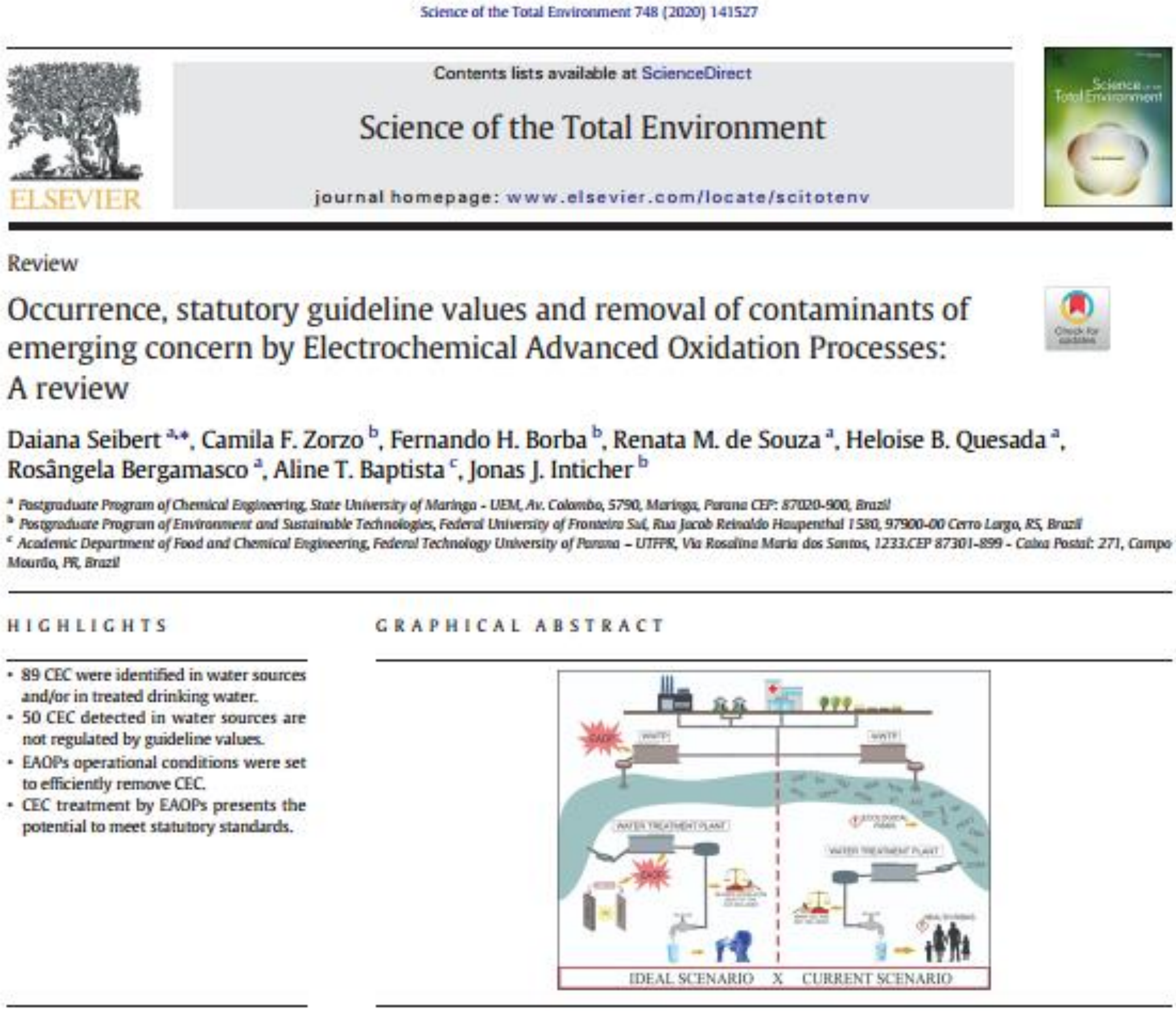
ABSTRACT

Micropollutants, also called emerging contaminants, consist of an extensive group of synthetic and natural substances, including pharmaceuticals, personal care products, steroid hormones, and agrochemicals. Currently, the monitoring of residual pharmaceuticals in the environment has been highlighted due to the fact that many of these substances are found in wastewater treatment plants effluents and surface waters, in concentrations ranging from ng L^{-1} to μg L^{-1}. Most of these compounds are discharged into the environment continuously through domestic sewage treatment systems. In the present work, it is presented an overview of water pollution by these pollutants, as well as a review of the recent literature about the use of low-cost adsorbents for the removal of the main pharmaceuticals found in surface water, focusing on municipal and agroindustrial wastes as precursors. It was possible to observe several examples of high adsorption capacities of these compounds with such materials, however other aspects must be considered in order to evaluate the real applicability in water and wastewater treatment, such as competition, recyclability and production cost.

Artigo 2



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Review

Occurrence, statutory guideline values and removal of contaminants of emerging concern by Electrochemical Advanced Oxidation Processes: A review

Daiana Seibert [a,*], Camila F. Zorzo [b], Fernando H. Borba [b], Renata M. de Souza [a], Heloise B. Quesada [a], Rosângela Bergamasco [a], Aline T. Baptista [c], Jonas J. Inticher [b]

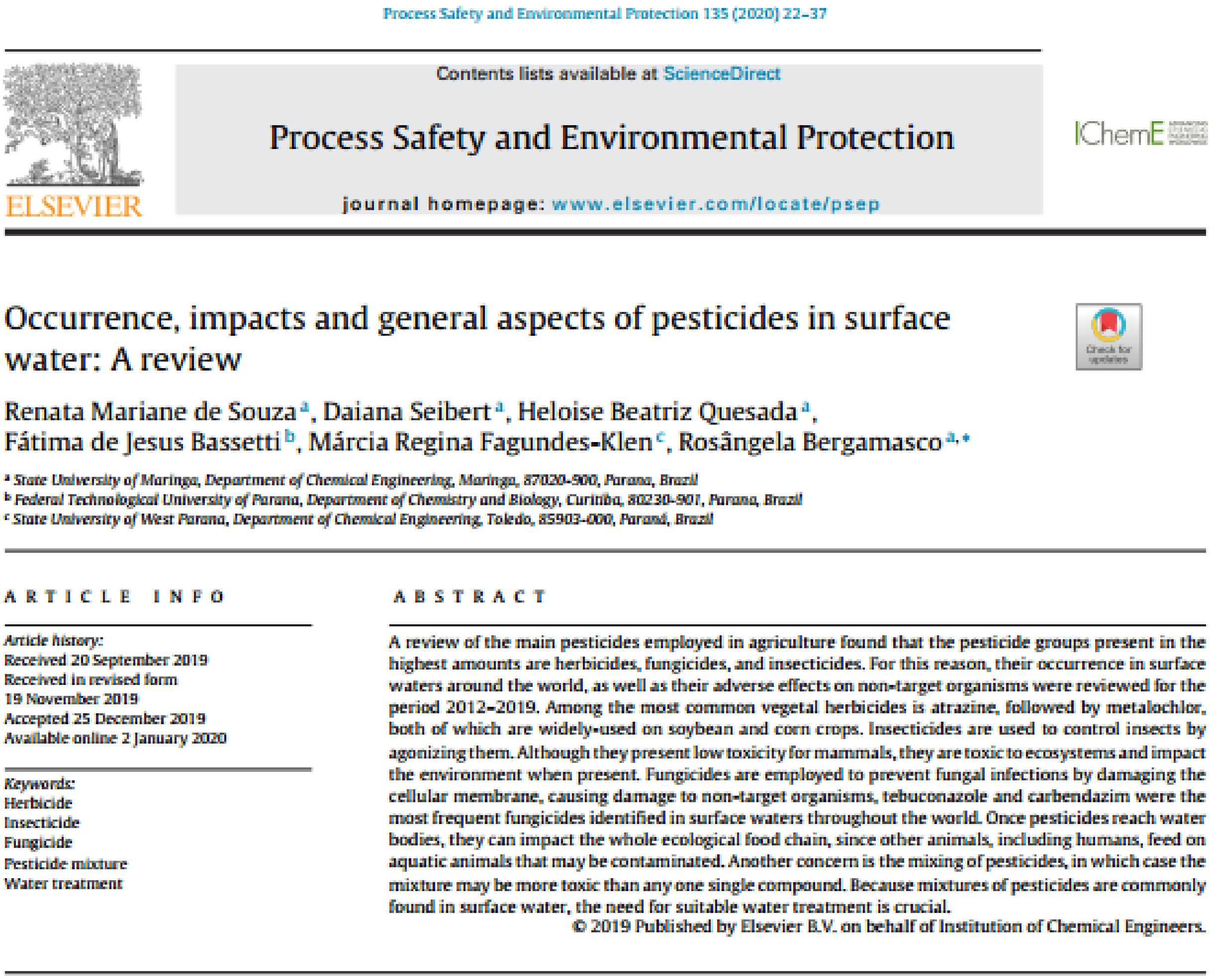
[a] *Postgraduate Program of Chemical Engineering, State University of Maringa - UEM, Av. Colombo, 5790, Maringa, Parana CEP: 87020-900, Brazil*
[b] *Postgraduate Program of Environment and Sustainable Technologies, Federal University of Fronteira Sul, Rua Jacob Reinaldo Haupenthal 1580, 97900-00 Cerro Largo, RS, Brazil*
[c] *Academic Department of Food and Chemical Engineering, Federal Technology University of Parana – UTFPR, Via Rosalina Maria dos Santos, 1233.CEP 87301-899 - Caixa Postal: 271, Campo Mourão, PR, Brazil*

HIGHLIGHTS

- 89 CEC were identified in water sources and/or in treated drinking water.
- 50 CEC detected in water sources are not regulated by guideline values.
- EAOPs operational conditions were set to efficiently remove CEC.
- CEC treatment by EAOPs presents the potential to meet statutory standards.

GRAPHICAL ABSTRACT

Artigo 3



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Occurrence, impacts and general aspects of pesticides in surface water: A review

Renata Mariane de Souza[a], Daiana Seibert[a], Heloise Beatriz Quesada[a], Fátima de Jesus Bassetti[b], Márcia Regina Fagundes-Klen[c], Rosângela Bergamasco[a,*]

[a] *State University of Maringa, Department of Chemical Engineering, Maringa, 87020-900, Parana, Brazil*
[b] *Federal Technological University of Parana, Department of Chemistry and Biology, Curitiba, 80230-901, Parana, Brazil*
[c] *State University of West Parana, Department of Chemical Engineering, Toledo, 85903-000, Paraná, Brazil*

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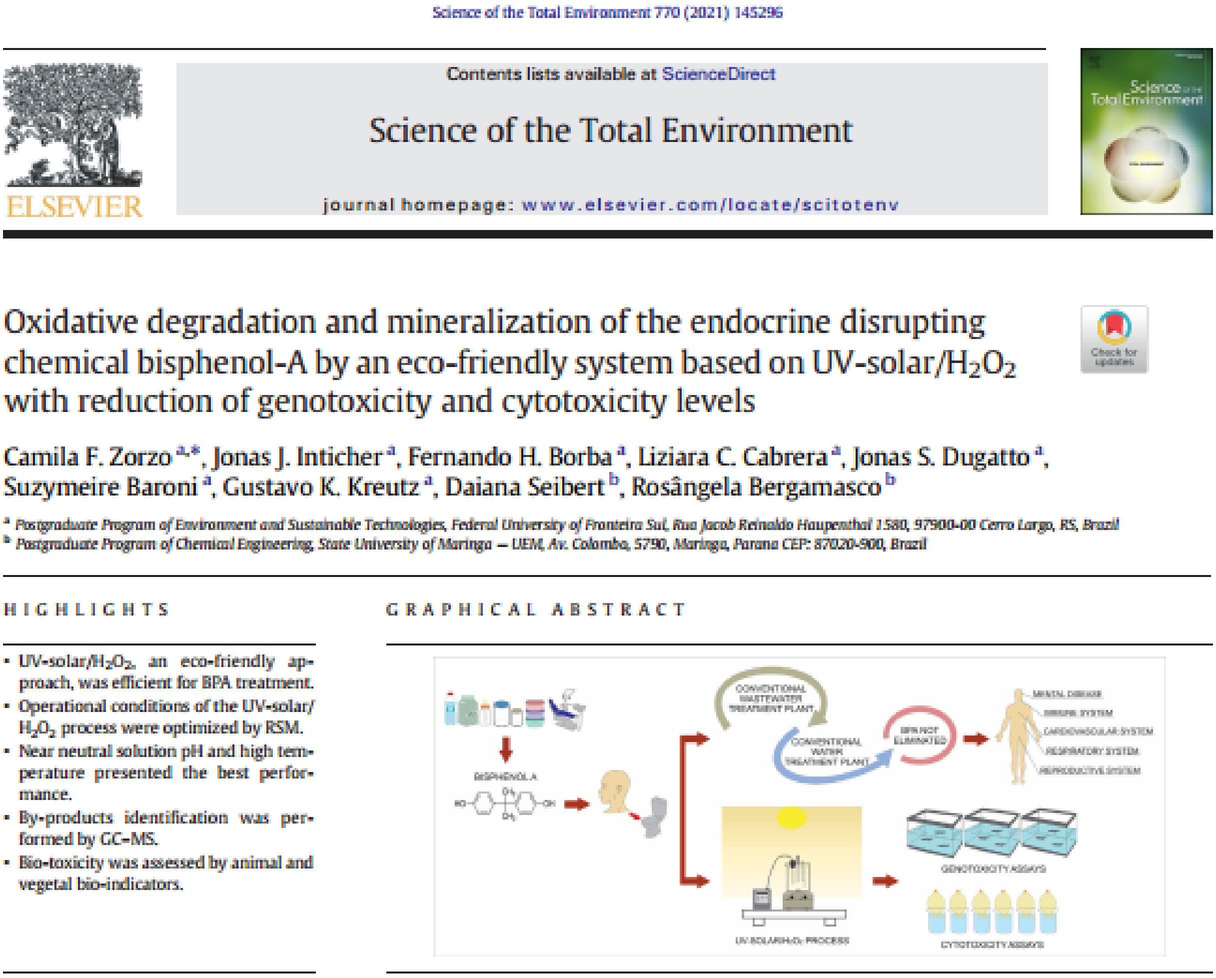
ABSTRACT

A review of the main pesticides employed in agriculture found that the pesticide groups present in the highest amounts are herbicides, fungicides, and insecticides. For this reason, their occurrence in surface waters around the world, as well as their adverse effects on non-target organisms were reviewed for the period 2012–2019. Among the most common vegetal herbicides is atrazine, followed by metalochlor, both of which are widely-used on soybean and corn crops. Insecticides are used to control insects by agonizing them. Although they present low toxicity for mammals, they are toxic to ecosystems and impact the environment when present. Fungicides are employed to prevent fungal infections by damaging the cellular membrane, causing damage to non-target organisms, tebuconazole and carbendazim were the most frequent fungicides identified in surface waters throughout the world. Once pesticides reach water bodies, they can impact the whole ecological food chain, since other animals, including humans, feed on aquatic animals that may be contaminated. Another concern is the mixing of pesticides, in which case the mixture may be more toxic than any one single compound. Because mixtures of pesticides are commonly found in surface water, the need for suitable water treatment is crucial.

Artigo 4



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Oxidative degradation and mineralization of the endocrine disrupting chemical bisphenol-A by an eco-friendly system based on UV-solar/H_2O_2 with reduction of genotoxicity and cytotoxicity levels

Camila F. Zorzo[a,*], Jonas J. Inticher[a], Fernando H. Borba[a], Liziara C. Cabrera[a], Jonas S. Dugatto[a], Suzymeire Baroni[a], Gustavo K. Kreutz[a], Daiana Seibert[b], Rosângela Bergamasco[b]

[a] Postgraduate Program of Environment and Sustainable Technologies, Federal University of Fronteira Sul, Rua Jacob Reinaldo Haupenthal 1580, 97900-00 Cerro Largo, RS, Brazil
[b] Postgraduate Program of Chemical Engineering, State University of Maringa – UEM, Av. Colombo, 5790, Maringa, Parana CEP: 87020-900, Brazil

HIGHLIGHTS

- UV-solar/H_2O_2, an eco-friendly approach, was efficient for BPA treatment.
- Operational conditions of the UV-solar/H_2O_2 process were optimized by RSM.
- Near neutral solution pH and high temperature presented the best performance.
- By-products identification was performed by GC–MS.
- Bio-toxicity was assessed by animal and vegetal bio-indicators.

GRAPHICAL ABSTRACT

APÊNDICE B – ARTIGO RESULTANTE DA PESQUISA DE INTERCÂMBIO

O seguinte artigo será submetido a revista internacional Process Safety and Environmental Protection.

Application of cork from stoppers as adsorbent for water and wastewater treatment using Ciprofloxacin as pharmaceutical model

Daiana Seibert[1,2♣], Helena P. Felgueiras[2], Fernando H. Borba[4], Natália C. Homem[2,3], Rosângela Bergamasco[1]

[1]*Postgraduate Program of Chemical Engineering, State University of Maringa, UEM, Av. Colombo, 5790 Maringa, Parana CEP: 87020-900, Brazil*

[2]*Centre for Textile Science and Technology (2C2T), University of Minho, Campus de Azurém, 4800-058, Guimarães, Portugal.*

[3]*Digital Transformation CoLAB (DTx), University of Minho, Campus de Azurém, Building 1, 4800-058, Guimarães, Portugal.*

[4]*Postgraduate Program of Environment and Sustainable Technologies, Federal University of Fronteira Sul, Rua Jacob Reinaldo Haupenthal 1580, 97900-00 Cerro Largo, RS, Brazil*

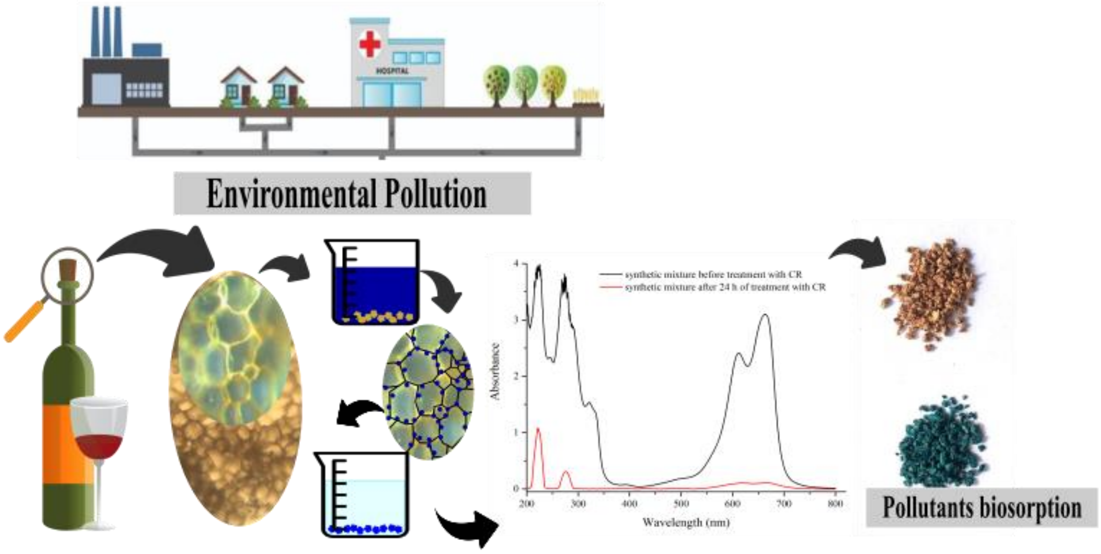
[♣] Corresponding author

E-mail: daiaseibert@hotmail.com

Highlights

Cork is an eco-friendly and cost-effective material;
Cork obtained from stoppers requires only a washing step before using;
High CEC removal was reached using cork as biosorbent;
As an absorbent material, cork can be potentially useful in water and wastewater treatments;
Heterogeneous CIP adsorptive process.

Graphical Abstract



Abstract

The worries around environmental pollution caused by contaminants of emerging concern (CEC) and the quality state of the water that reaches our homes are becoming more evident. In this regard, the present study investigated the biosorption efficiency of cork, collected from wine stoppers, against the antibiotic ciprofloxacin (CIP), contained within a synthetic mixture made of atrazine (ATZ), bisphenol A (BPA) and methylene blue (MB). The cork adsorbent was characterized for its functional groups via Fourier Transform Infrared spectroscopy (FTIR), for its point of zero charge (pH_{pzc}) by pH meter, and for its morphology via brightfield microscopy. The effect of temperature (25, 35 and 45 ºC), pH (3.0, 7.0 and 9.0), adsorbent mass (0.25, 0.5 and 0.75 g), CIP initial concentration (5, 25 and 50 mg L^{-1}), and presence of ions ($MgCl_2$, KCl, Na_2SO_4, $CaCl_2$) within the testing solution was evaluated for CIP adsorption onto cork. Even though it followed the pseudo-second-order and the Elovich kinetic models, the isotherm data fitted better the Freundlich model, suggesting a heterogeneous adsorptive process. Maximum adsorption capacity of 2.88 mg g^{-1} was reached at 25 ºC, solution pH 7.0, using 0.25 g raw cork (CR) with a CIP initial concentration of 25 mg L^{-1}. CR regeneration was studied after five cycles of adsorption/desorption. Then, the potential of the adsorbent for the wastewater treatment was evaluated. This manuscript showed that cork from stoppers present double environmental interest, since it may act improving waste management and is a promising adsorbent material for water and wastewater treatment, contributing to public health and environmental protection.

Keywords: eco-friendly adsorbent; low-cost strategy; contaminants of emerging concern; synthetic effluent; heterogeneous adsorption.