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NAIRA DELL'OSBEL

TRATAMENTO DE EFLUENTES URBANOS UTILIZANDO *WETLANDS* CONSTRUÍDOS HÍBRIDOS PARA REMOÇÃO DE NUTRIENTES COM BARREIRA ADSORVENTE REMOVÍVEL

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Dissertação apresentada ao Programa de Pós-Graduação em Tecnologia Ambiental , Universidade de Santa Cruz do Sul – UNISC, como requisito parcial para o título de Mestre em Tecnologia Ambiental.

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Dra. Lourdes Teresinha Kist
Universidade de Santa Cruz do Sul – UNISC

Dra. Lucia Helena Ribeiro Rodrigues
Universidade Federal do Rio Grande do Sul – UFRGS

Dr. Ênio Leandro Machado
Universidade de Santa Cruz do Sul - UNISC
Orientador

Santa Cruz do Sul, 2020.

“*A vida baseada no Amor incondicional gera abundância*”.

(Ernst Götsch)

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RESUMO

O gerenciamento de recursos deve seguir um fluxo circular para que substâncias importantes como o fósforo não sejam desperdiçadas na forma de poluentes de corpos d'água. Portanto, o objetivo deste estudo foi investigar inovações com foco na recuperação de fósforo em *wetlands* construídos (WC), bem como mecanismos de remoção relacionados e o desenvolvimento e aplicação mais recente de novos substratos com alta eficiência de remoção e potencial de recuperação de fósforo. Por meio da análise bibliométrica, foram identificadas as vias de remoção de P mais importantes, concluindo que a escolha do substrato é um dos principais aspectos a serem considerados quando se visa a remoção de fósforo, e muitas melhorias foram obtidas através da aplicação de materiais de origem natural e artificial, bem como resíduos de construção e subprodutos de processos industriais. Assim, é importante que os materiais escolhidos para um substrato de WCs tenham afinidade com o fósforo, possibilidade de reciclagem, baixo custo e disponibilidade local, de forma a se aproximar dos conceitos de economia circular e desenvolvimento sustentável.

Palavras-chave: Recuperação de fósforo. *Wetlands* construídos. Economia circular. Bibliometria

WASTEWATER TREATMENT USING HYBRID CONSTRUCTED WETLANDS FOR REMOVAL OF NUTRIENTS WITH REMOVABLE ADSORBENT BARRIER

ABSTRACT

Abstract Resource management should follow a circular flow so that important substances such as phosphorous are not wasted in the form of water bodies pollutants. Therefore, the objective of this study was to investigate innovations focussing on the recovery of phosphorous in constructed wetland (CW), as well as related removal mechanisms and the more recent development and application of new substrates with high removal efficiency and potential for phosphorus recovery. Using bibliometric analysis, the most important P removal pathways were identified, concluding that substrate choice is one of the main aspects to be considered when aiming for phosphorous removal, and many improvements were obtained through the application of materials from either natural and artificial origins, as well as construction waste and by-products of industrial processes. Thus, it is important that the chosen materials for a wetland substrate must present affinity with phosphorous, recycling possibility, low cost and local availability, in order to approach the concepts of circular economy and sustainable development.

Keywords: Phosphorus recovery. Constructed wetlands. Circular economy. Bibliometrics.

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TABELA ARTIGO 1

LISTA DE ABREVIATURAS

APHA	*American Public Health Association*
AWWA	*American Water Works Association*
COT	Carbono Orgânico Total
CI	Carbono Inorgânico
CT	Carbono Total
ETE	Estação de Tratamento de Efluentes
FTW	*Floating Treatment Wetland*
NT	Nitrogênio Total
NTK	Nitrogênio Total Kjeldahl
PEMD	Polietileno de Média Densidade
PT	Fósforo Total
STD	Sólidos Totais Dissolvidos
UASB	*Upflow Anaerobic Sludge Blanket*
WCs	*Wetlands* Construídos
WCFSH	*Wetland* Construído de Fluxo Subsuperficial Horizontal
WCFV	*Wetland* Construído de Fluxo Vertical

LISTA DE ABREVIATURAS ARTIGO 1

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
CW	Constructed Wetland
LECA	Light Expanded Clay Aggregate

LISTA DE ABREVIATURAS ARTIGO 2

APHA	American Public Health Association
AWWA	American Water Works Association
CO_2	Dióxido de Carbono
COT	Carbono Orgânico Total
CI	Carbono Inorgânico
CT	Carbono Total
ETE	Estação de Tratamento de Efluentes
FTW	Floating Treatment Wetland
NT	Nitrogênio Total
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PEMD	Polietileno de Média Densidade
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SUMÁRIO

1 INTRODUÇÃO

O fósforo e o nitrogênio são nutrientes que ocorrem naturalmente, porém quando em excesso em ecossistemas aquáticos diminuem a sua qualidade (ZIEGLER, 2016). Nestas circunstâncias há um aumento na proliferação de espécies vegetais oportunistas adaptadas as novas condições ambientais, substituindo espécies inicialmente presentes e causando uma elevada produção de biomassa, de modo que a sua degradação pelas bactérias diminui o oxigênio disponível no meio aquático, produz emissões tóxicas (CO_2, H_2S e CH_4), favorece a perda de biodiversidade, produção de toxinas por alguns tipos de algas e muitas vezes até a morte de organismos aquáticos que necessitam de mais oxigênio (LE MOAL et al., 2019).

Os sistemas de tratamento de águas residuais convencionais como os tanques *Imhoff* e tanques sépticos não são capazes de remover eficientemente nitrogênio, fósforo e organismos patogênicos, por isso devem ser utilizados antes de um tratamento secundário (MASSOUD et al., 2009). Além disto, atualmente há um grande interesse em controlar a quantidade de nutrientes como o fósforo, que é lançado em águas superficiais por meio da descarga de efluentes domésticos, industriais e de escoamento superficial.

Devido à mineração insustentável e a possível escassez futura de fósforo, isto vem estimulando o desenvolvimento de metodologias para a recuperação do mesmo a partir dos efluentes (METCALF e EDDDY, 2016). Este aspecto é fundamental para a sustentabilidade referenciada com as propostas dos Objetivos do Desenvolvimento Sustentável (ODS), principalmente com o objetivo 6 (Água Limpa e Saneamento) que visa assegurar a disponibilidade e gestão sustentável da água e saneamento para todos (Organização das Nações Unidas, 2016).

Neste sentido, as propostas dos ODSs devem ser associadas às tecnologias limpas, especialmente no item da gestão das águas, pois aborda o conceito da economia circular, tão necessária no cenário atual, onde é preciso recuperar energia, nutrientes, realizar integração paisagística, recuperar áreas degradadas e reutilizar eficazmente águas residuais (COLARES et al., 2019).

Entretanto, o Brasil carece em muito de saneamento, sendo que aproximadamente 40% do esgoto gerado no país é tratado As configurações mais adotadas em estações de tratamento no Brasil são lagoas anaeróbias seguidas de lagoas facultativas; reatores UASB; lodos ativados; lagoas de configurações mistas e fossas sépticas seguidas de filtros anaeróbios. O Brasil oferece condições climáticas favoráveis ao tratamento biológico de esgotos e a tendência atual é a utilização de reatores UASB seguidos por alguma forma de pós-tratamento (VON SPERLING, 2016), tendo uma configuração que pode ser adequada para cerca de 95% dos munícipios brasileiros, os quais são de pequeno ou médio porte (≤100.000 habitantes). No entanto, pesquisar e aplicar tecnologias complementares, potencialmente utilizáveis em unidades descentralizadas para reduzir os impactos eutrofizantes dos corpos d’água, também merece atenção.

Os *Wetlands* Construídos (WCs) são áreas úmidas projetadas para o tratamento de águas residuais ou para contenção de água da chuva, eles são preenchidos com substrato que pode ser um material natural, artificial ou residual e vegetado com plantas adaptadas a ambientes saturados de água e rico em nutrientes.

Neste sentido, os WCs são projetados para a remoção de nutrientes e outros contaminantes dos efluentes, observando o que ocorre na natureza, representando uma alternativa sustentável para o tratamento de efluentes, sendo indicados para o tratamento descentralizado de esgotos especialmente em pequenas comunidades e locais distantes (KUMAR e DUTTA, 2019).

A remoção de fósforo em WCs é limitada devido ao uso de materiais filtrantes com baixa capacidade de sorção. Já a de nitrogênio é afetada pelas condições anóxicas/anaeróbias em leitos de filtração que não permitem a nitrificação do íon amônio. A combinação de WCs híbridos mais utilizados são os de fluxo vertical e fluxo horizontal, que são usados para melhorar as remoções, principalmente, de nitrogênio. Sendo que os sistemas de fluxo vertical favorecem a nitrificação e os de fluxo horizontal a desnitrificação (VYMAZAL, 2005).

Em sistema de WCs híbridos, combinando os fluxos de sistemas *floating* e de fluxo horizontal, preenchidos com seixos, *ceramsite* (areia artificial porosa) e brita, Abbasi et al., (2019) observaram que a maior parte da remoção do fósforo total ocorreu no leito da matriz, enquanto que a remoção de nitrogênio esteve mais relacionada ao sistema radicular das plantas e a biomassa, sendo que o nitrogênio total (NT) e o amoniacal ($NH_{4'}$) tiveram remoção maior no verão.

O processo de adsorção pela incorporação de substratos em WCs é uma das melhores alternativas para a remoção de fósforo e recentemente vários materiais naturais e artificiais têm apresentado potencial para a aplicação desta tecnologia em pequena escala (BUNCE, 2018). Para remoção de fósforo, por exemplo, Lima et al. (2018) obtiveram média de 87% de remoção com tijolos quebrados; Bolton et al. (2019) alcançaram média de 94,3% com biochar e Ge et al. (2019) obtiveram média de remoção de P total de 87,7% com pirita natural.

Um sistema de tratamento vegetado em policultura melhora a paisagem, a qualidade do *habitat* para a comunidade e a resistência ao estresse ambiental (Leiva et al., 2018). Uma policultura fornece vários benefícios ecológicos, já que, o número de espécies vegetais e a complexidade estrutural dos ecossistemas geralmente tem correlação com a riqueza de espécies da fauna silvestre. Por isso monoculturas ou comunidades com uma única espécie dominante têm valor ecológico limitado (KADLEC & WALLACE, 2009).

Letourneau et al. (2011) encontraram um efeito benéfico no uso de esquemas de diversificação vegetal na supressão de herbívoros, aumentando seus inimigos naturais e reduzindo danos na colheita. Em estudo realizado no Jardim Botânico da Universidade Estadual de Oklahoma por Bonner et al (2015), encontraram maior abundância de inimigos naturais e polinizadores em policulturas quando em comparação às monoculturas, sugerindo este tipo de cultivo como forma de melhorar a saúde e a reprodução das plantas.

Os WCs podem trazer diversos benefícios econômicos aliados ao tratamento de efluente. Em estudo realizado na comunidade de Villagrán, no município de Ixmiquilpan, no centro do México, foi desenvolvido um sistema de tratamento de efluentes que produz flores que são comercializadas no mercado local, utilizando água tratada em piscicultura para a produção de *Oreochromis niloticus* (BELMONT et al., 2018).

A produção de flores em WCs é benéfica do ponto de vista econômico pois, abre a possibilidade de comercialização das mesmas, podendo contribuir para que essas ecotecnologias sejam aceitas com maior impacto paisagístico em sociedades onde se faz necessária esse tipo de solução (SANDOVAL-HERAZO et al., 2018).

É necessário utilizar processos que possibilitem a redução do potencial eutrofizante e incentivem a reutilização da água, porém além de todos os ganhos ambientais associados aos WCs os requisitos de área associados aos fatores de carga para NTK e P total podem dificultar o uso desses sistemas, por isso é importante a utilização de processos de pré-tratamento (HORN et al., 2014). Silveira et al. (2019) utilizaram processo anaeróbio (tanque de armazenamento de efluente) e microalgas como tratamento preliminar ao sistema de WCs, alcançando médias de remoção de 58% para demanda bioquímica de oxigênio, 63% para fósforo total e 100% para nitrogênio amoniacal. Assim como Colares et al. (2019), que utilizaram reatores anaeróbios seguidos de WCs híbridos+ozonização, alcançando eficiências médias de remoção de 78,9% para matéria orgânica carbonácea, 91% para nitrogênio, 96,7% para cor aparente, 99,1% para turbidez e 75% para fósforo nos primeiros 8 meses de operação do sistema.

Diante dos desafios e avanços identificados na área de tratamento de efluentes, estabeleceu-se como objetivo do presente trabalho o desenvolvimento de sistema de tratamento de efluentes domésticos utilizando WCs híbridos com elevada capacidade de remoção de nutrientes, valor paisagístico e ecológico associado através da utilização de policultura de plantas ornamentais e ainda alcançar padrão de qualidade do efluente que permitisse reuso.

2 OBJETIVOS

2.1 Objetivo Geral

Desenvolver sistema de *Wetlands* Construídos Híbridos com capacidade de remoção de nutrientes e valor paisagístico através da utilização de plantas ornamentais.

2.2 Objetivos específicos

- Avaliar o desempenho de barreiras filtrantes/adsorventes removíveis na diminuição do potencial eutrofizante do efluente;
- Analisar o desempenho de sistema híbrido com múltiplos estágios em série;
- Avaliar o desempenho de sistema *Floating* com ilhas de fitorremediação para a avaliação de adaptabilidade de diversas espécies;
- Avaliar o enquadramento para reuso do efluente tratado no sistema.

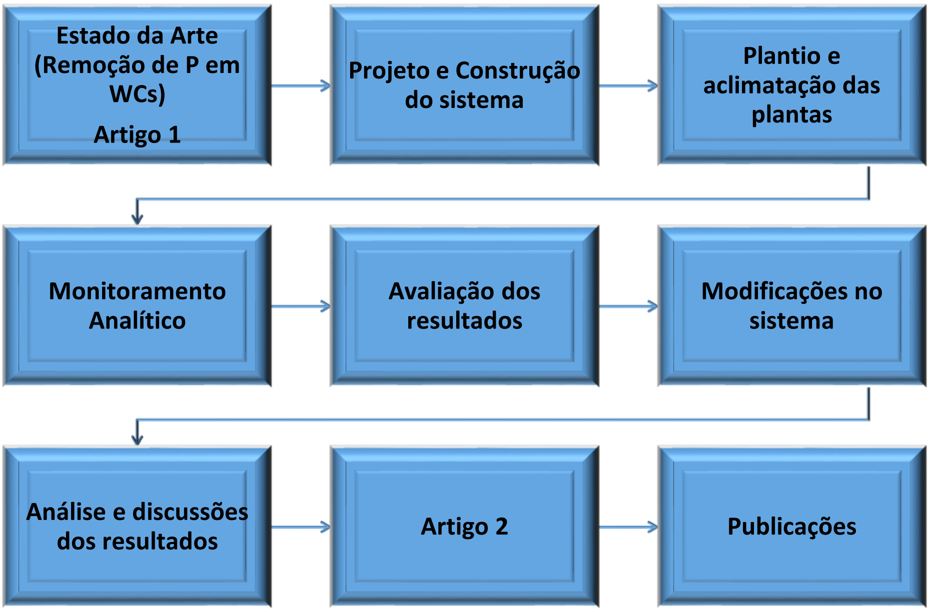
3 METODOLOGIA

3.1 Local do estudo e sistema de WCs Híbridos desenvolvido

Foi realizado primeiramente uma pesquisa bibliométrica e bibliográfica para aprofundamento dos conhecimentos na área de *Wetlands* Construídos, principalmente no que diz respeito a remoção de fósforo (P) que era um dos principais focos do trabalho. Para isto foi utilizado a Base de dados do *Web of Science* para obtenção de dados para trabalho dentro do *Software VOSviewer* para a realização da bibliometria.

Na Figura 1 está apresentada o fluxograma das principais etapas de desenvolvimento do presente trabalho.

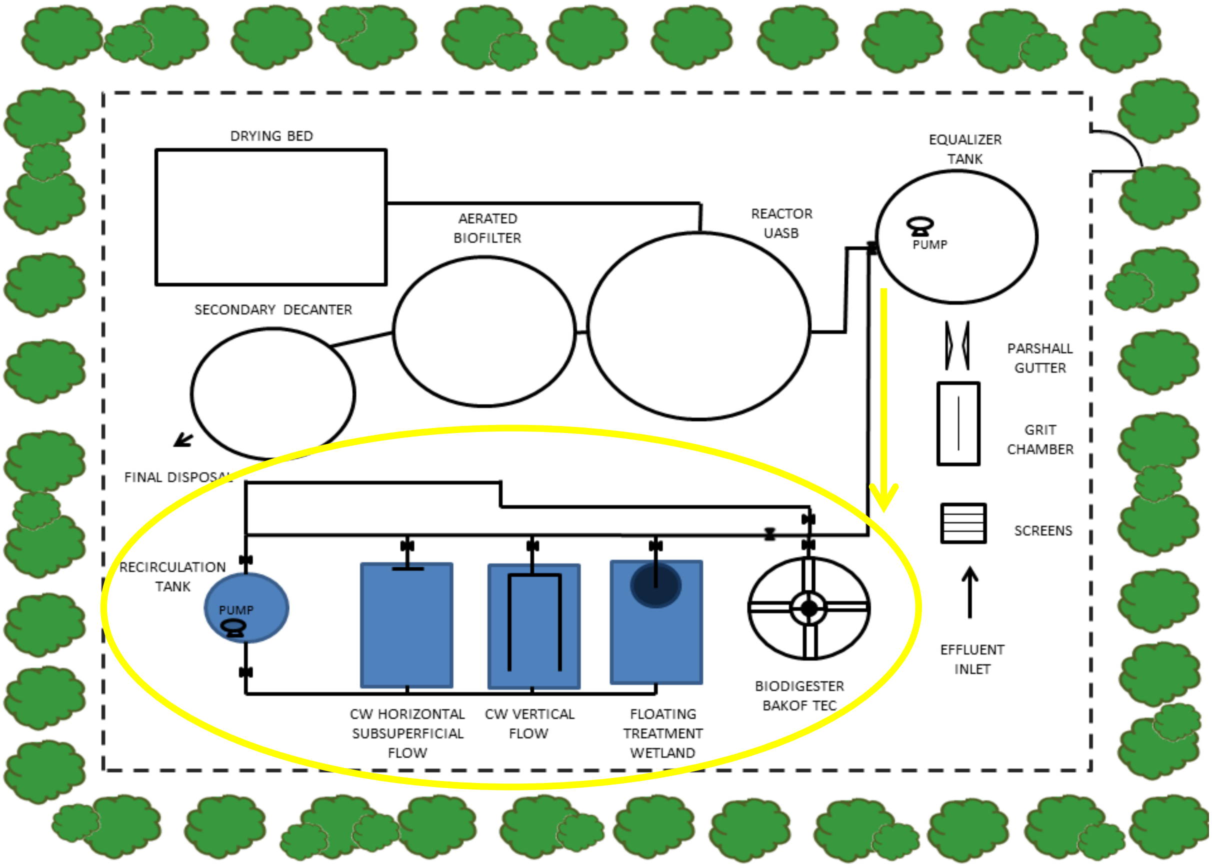
Figura 1 - Fluxograma das principais etapas da pesquisa.



Fonte: Autora.

A pesquisa foi realizada dentro da Estação de Tratamento de Efluentes (ETE) e dos Laboratórios de Pesquisa do Campus da Universidade de Santa Cruz do Sul (UNISC), município de Santa Cruz do Sul – RS. Na Figura 2 está apresentado o esquema das etapas principais da pesquisa. A parte destacada em amarelo na Figura 2 representa o sistema de biodigestão e WCs híbridos desenvolvidos no presente trabalho, sendo realizado durante o período de setembro de 2018 a dezembro de 2019. Nos meses de setembro e outubro de 2018 foi realizada a colocação das caixas, o preenchimento e o plantio das macrófitas.

Figura 2 – Esquema geral do local de estudo.



Fonte: Autora, 2019.

O efluente utilizado era oriundo de mictórios e banheiros da Universidade, sendo que este é gerado a uma vazão média de 103,2 m^3dia^{-1} (Silveira et al., 2017) e é encaminhado para tratamento na ETE da Unisc que conta com sistema de gradeamento, desarenador, tanque equalizador, reator anaeróbio de fluxo ascendente, biofiltro aerado e um decantador final.

No início foi realizada uma diluição do efluente, começando com 10%, depois 25%, 50%, 75% e por fim 100% de efluente para que houvesse o mínimo possível de estresse às plantas neste período de aclimatação, o que foi muito benéfico, pois não houve morte de nenhum indivíduo. O monitoramento analítico começou no mês de dezembro de 2018.

Na configuração do sistema proposto o efluente passava pelas etapas de gradeamento, desarenador e tanque equalizador antes de entrar no sistema desenvolvido no presente estudo. Logo após era bombeado para um biodigestor da marca Bakof Tec onde ficava retido por 3 dias para então ser enviado por gravidade para a o FTW constituído por um decantador primário e ilhas flutuantes de tratamento.

Depois desta etapa o efluente segue para um WC de fluxo vertical preenchido com brita e após para um WC de fluxo horizontal que possui uma barreira adsorvente removível preenchida com tijolos de argila quebrados e então segue para o descarte final no Arroio Lajeado.

O Biodigestor é constituído por um tanque em polietileno de média densidade (PEMD), sendo composto por um reator anaeróbio de fluxo ascendente e um filtro anaeróbio de fluxo ascendente de 1,45 m^3 de volume, tempo de detenção hidráulica de 3 dias e 1,25 m de diâmetro por 1,79 m de altura.

Após passar pelo biodigestor, o efluente segue para o sistema de *floating treatment wetland* que é constituído por um decantador primário para retirada de sólidos e por 15 ilhas flutuantes de tratamento de 15 cm de diâmetro e 10 cm de altura, sendo 3 ilhas vegetadas com *Canna x generalis*, 3 ilhas com *Equisetum sp.*, 3 ilhas com *Chrysopogon zizanioides*, 3 ilhas com *Hymenachne grumosa* e 3 ilhas com *Cyperus papyrus nanus*.

Depois de passar pela etapa de tratamento no *Floating Treatment Wetland*, o efluente segue para a etapa de WC de fluxo vertical, sendo que esta caixa possui um volume útil de 360 L e foi preenchida com 3 graduações diferentes de brita, sendo esta caixa vegetada pelas espécies *Canna x generalis, Chrysopogon zizanioides e Xanthosoma violaceum.*

A última etapa é constituída por um WC de fluxo subsuperficial horizontal, com um volume útil de 360 L e vegetada com as espécies *Cyperus papyrus nanus*, *Strelitzia reginae, Canna x generalis* e *Hymenachne grumosa*. Esta caixa foi preenchida com graduações diferentes de brita, sendo que nas áreas de entrada e saída do efluente foram utilizadas britas de tamanho maiores para evitar o entupimento da tubulação. Nessa caixa foi utilizada uma barreira filtrante constituída por cestos removíveis preenchidas com tijolos de argila quebrados com o objetivo de obter eficiência na remoção de fósforo e aumento na vida útil dos sistemas.

Optou-se pelo cultivo de espécies variadas com potencial paisagístico e adaptadas ao ambiente de *Wetlands* Construídos, assim como Calheiros et al. (2015) que utilizaram uma policultura de plantas ornamentais, de forma a melhorar a aparência estética do WC e a sua biodiversidade.

A densidade inicial de plantas no sistema FTW foi de 5 plantas/m^2, no WCFV foi de 13 plantas/m^2 e no WCFSH foi de 7 plantas/m^2. A tubulação utilizada em todo o sistema foi de 40 mm e foram feitos furos de 8 mm na tubulação de entrada e coleta do efluente. No tanque de recirculação há uma bomba submersa de capacidade máxima de 125 L min^{-1}, a mesma faz o bombeamento do efluente de uma etapa à outra.

Como complementação foi realizado estudo e bibliométrico como metodologia para guiar a pesquisa, ampliar os conhecimentos na área e conhecer os atuais avanços na área, principalmente no que diz respeito a remoção de P em WCs e a importância na recuperação de recursos, conforme Artigo 1.

3.2 Caracterizações analíticas

A caracterização analítica foi realizada durante o período de um ano, sendo analisados parâmetros físico-químicos e biológicos a cada 7 dias. Foram analisados 5 pontos de coleta: efluente bruto do equalizador, efluente após biodigestor, efluente após WCFLF, efluente após WCFV e efluente após WCFSH.

Os parâmetros analisados em cada uma das etapas do tratamento foram: demanda bioquímica de oxigênio (DBO_5), demanda química de oxigênio (DQO), carbono orgânico total (COT), carbono inorgânico (CI), carbono total (CT), nitrogênio amoniacal ($N\text{-}NH_3$), nitrogênio total Kjedahl (NTK), nitrogênio total (NT), fósforo solúvel ($P_{\text{solúvel}}$), fósforo total (P_{total}), condutividade, turbidez, sólidos totais dissolvidos (STD), sólidos sedimentáveis, potencial hidrogeniônico (pH), cor (absorbância 420 e 254 nm), alcalinidade, oxigênio dissolvido, temperatura, coliformes totais, *Escherichia coli*, biomassa e análise foliar de nutrientes. Na Tabela 1 estão apresentados os parâmetros analisados e os respectivos métodos e frequência de análise de cada um deles.

Tabela 1- Resumo dos parâmetros analisados, frequência de análise e métodos aplicados.

Parâmetro	**Frequência**	**Período de amostragem**	**Método aplicado**
DQO	Quinzenal	01/19 a 12/19	Titulação – Colorimétrico
DBO_5	Quinzenal	01/19 a 12/19	DBO após 5 dias à 20ºC
Coliformes T./ *E. coli*	Semestral	02/19 a 12/19	Placas Petrifilm 3M®
NT	Mensal	06/19 a 12/19	Shimadzu TOC-L
NTK	Semanal	03/19 a 05/19	Destilação – Titulação
$N\text{-}NH_3$	Quinzenal	01/18 a 12/19	Destilação – Titulação
COT/CI/CT	Mensal	06/19 a 12/19	Shimadzu TOC-L
P solúvel	Quinzenal	01/18 a 12/19	Colorimétrico
P total	Quinzenal	03/19 a 12/19	Colorimétrico
Alcalinidade	Bimestral	02/19 a 12/19	Colorimétrico e titulométrico
Oxigênio Dissolvido	Semanal	12/18 a 12/19	Potenciométrico

Temperatura	Semanal	07/19 a 12/19	Potenciométrico
Sólidos Sedimentáveis	Mensal	01/19 a 12/19	Cone Inhoff
Condutividade	Semanal	12/18 a 12/19	Eletroquímico
STD	Semanal	12/18 a 12/19	Eletroquímico
pH	Semanal	12/18 a 12/19	Potenciométrico
Cor	Semanal	12/18 a 12/19	Colorimétrico (λ= 420 e 254 nm)
Turbidez	Semanal	12/18 a 12/19	Método ótico
Comprimento das raízes	-	-	Medição com trena
Biomassa	Trimestral	03/19 a 12/19	Silveira (2010)
Análise de macro e micro nutrientes	-	10/19	Digestão assistida por micro-ondas e determinação espectrométrica por plasma de argônio através de ICP/OES

Fonte: Autora.

A caracterização da biomassa foi realizada pelo corte da parte aérea a uma altura de 20 cm acima da superfície do substrato a cada 4 meses, sempre observando o momento em que não há mais crescimento visível, onde ela atinge seu ápice. Era feita a pesagem em balança granatária da massa úmida e da massa seca após secagem em estufa bacteriológica a 65°C até peso constante conforme metodologia descrita por Silveira (2010). Foi acompanhado também o crescimento de raízes e a acumulação de nutrientes na parte aérea (acima de 20 cm do suporte) através de análise foliar.

A caracterização analítica seguiu os padrões descritos na *Standard Methods for the Examination of Water and Wastewater* - APHA/AWWA (2012). As análises de COT, CT, CI, e NT foram realizadas no Núcleo Tecnológico de Oleoquímica e Biotecnologia da UNISC que utiliza equipamento Shimadzu TOC-L com oxidação catalítica por combustão a 680 ºC com injeção de ar seguido de detecção com infravermelho não dispersivo. A análise de cor 254 nm foi realizada no Laboratório de Instrumentação Analítica, a análise de macro e micro nutrientes foi realizada através de contratação de serviços junto a Central Analítica da Unisc e as demais análises foram realizadas no Laboratório de Análise de Tratamento de Água e Efluentes.

As plantas utilizadas no presente estudo foram coletadas em locais próximos a área de estudo, algumas dentro do campus da universidade e outras em locais nos arredores, sendo que apenas a *Cyperus prolifer* e a *Strelitzia reginae* foram compradas em floriculturas.

4 ARTIGO 1

Recovering Wastewater Phosphorous through Constructed Wetlands: Current Scenario and Development of New Alternatives

SITUAÇÃO ATUAL NO MOMENTO DA DEFESA: Publicado na Revista Water, Air and Soil Pollution

Naira Dell'Osbel[1], Gustavo Stolzenberg Colares[1], Gislayne Alves Oliveira[2], Maiara Priscilla de Souza[1], Carolina Vieira Barbosa[1], Ênio Leandro Machado[1]

1 - Programa de Pós-graduação em Tecnologia Ambiental – PPGTA, Universidade de Santa Cruz do Sul, RS, Brasil

2 - Programa de Pós-graduação em Recursos Hídrico e Saneamento Ambiental, Universidade Federal do Rio Grande do Sul, RS, Brasil

Abstract Resource management should follow a circular flow so that important substances such as phosphorous are not wasted in the form of water bodies pollutants. Therefore, the objective of this study was to investigate innovations focussing on the recovery of phosphorous in constructed wetland (CW), as well as related removal mechanisms and the more recent development and application of new substrates with high removal efficiency and potential for phosphorus recovery. Using bibliometric analysis, the most important P removal pathways were identified, concluding that substrate choice is one of the main aspects to be considered when aiming for phosphorous removal, and many improvements were obtained through the application of materials from either natural and artificial origins, as well as construction waste and by-products of industrial processes. Thus, it is important that the chosen materials for a wetland substrate must present affinity with phosphorous, recycling possibility, low cost and local availability, in order to approach the concepts of circular economy and sustainable development.

Keywords phosphorus recovery . constructed wetlands . circular economy . bibliometrics

1 Introduction

The release of high loads of phosphorous in water bodies results in the eutrophication process, and the production of fertilizers generate elevated amounts of carbon emission, radioactive by-products and heavy metal pollution. In addition, global reserves of phosphate rocks may be extinct in 50 to 100 years and the material quality is decreasing while the related production costs are growing (Cordell et al. 2009). Therefore, scarcity and environmental issues combined with the waste of phosphorous demand a new approach to resource management.

Phosphorous is a fundamental nutrient for all living organisms on Earth. Dependence on non-renewable sources brings high risk to the maintenance of the global food supply chain. For this reason, the recovery of wastewater flows can contribute to better practices of waste and water bodies pollution (Daneshgar et al. 2018). In addition, phosphorous recovery and recycling are being encouraged by concerns regarding inappropriate soil management, decreasing soil fertility and ensuring food safety (Roy 2016).

There are many efficient technologies in removing phosphorous. Yet, many of them present high costs and energy demand, complex operation and require excessive maintenance, such as activated sludge, photobioreactors and membrane bioreactors. Thus, constructed wetlands (CWs) with sorption filter media can provide an integral treatment solution, removing a variety of contaminants by precipitation, microbial activity and plant absorption processes (Bunce 2018).

CWs are systems projected for removing nutrients and other contaminants from wastewater, using naturally occurring processes, and thus representing a sustainable alternative for wastewater treatment, being indicated for decentralized treatment mainly in small communities and low-density areas. CWs have lower energy consumption, lower operating and maintenance costs, and provide habitat for diverse species, aquaculture, groundwater recharge, flood control, recreation area, and increased local landscape value (Kumar and Dutta 2019).

Adsorption processes are currently the most promising method for removing phosphorous, and the substrate is a feasible solution for efficient phosphorous removal. Recently, several materials have been developed and are emerging for the potential application of this technology at small scales (Bunce 2018). Some authors have efficiently applied alternative materials in CWs aiming for phosphorous removal. Lima et al. (2018) obtained 87% average removal using broken bricks; Bolton et al. (2018) reached an average of 94.3% with biochar and Ge et al. (2019) verified an average total P removal of 87.7% when using natural pyrite.

When selecting the material for the bed of a CWs, important aspects to consider are time until saturation, presence of heavy metals and recyclability of the filtering media as fertilizers after saturation (Vohla et al. 2011); this last factor can positively impact agricultural production by reducing the dependency on industrialized chemical fertilizers. An example would be the application of chemical fertilizers and pesticides in conventional rice production, which are the main factors of environmental impact from these activities; thus, organic rice production is a promising sustainable form precisely use of sustainable and alternative sources of phosphorous (He et al. 2018).

It is important the addition of a second treatment stage, after the CW is filtered specifically for phosphorous reduction. In a study performed by Adera et al. (2018), these types of filters were filled with steel slag which significantly improved soluble phosphorous removal, reaching almost 100% efficiency in a subsurface horizontal flow CW.

Phosphorous recovery through absorption by plants also is beneficial for biomass production. Matos et al. (2008) obtained removal efficiencies of almost 199 kg ha^{-1} y^{-1}of P in a CW when using Tifton 85 (*cynodon* spp), and recommend the potential biomass application for animal feeding due to its high nutritional value.

The objective of this bibliometric analysis was to better understand the mechanisms associated with the processes of removal and recovery of phosphorous from wastewater in order to approach circular economy requirements concerning nutrient recovery and discharge of wastewater with low eutrophication potential.

2 Material and Methods

The present review aims to focus on the main aspects related to phosphorous removal when using constructed wetland systems, field innovations and the most relevant topics. The performed bibliometric mapping allowed the identification of the most cited items in literature and the investigating of relationships between the terms obtained.

In order to analyse the state of art, a temporal bibliometric analysis was performed using information from the *Web of Science* platform. This database was used due to data quality and availability for usage analysis VOSviewer software, considering the entire period of records and all document types, and thus following the methodology described by De Souza et al. (2018).

According to the data obtained with bibliometric mapping, bibliographic research was conducted for the contextualisation of the investigated subject and search for recent scientific advances in the publications related to the subject focused in this study. The aim was to deepen the generated knowledge over the description and discussion of the main aspects related to phosphorous recovery though constructed wetlands.

3 Results and Discussion

3.1 Phosphorous in wastewater and constructed wetlands and its importance for circular economy

Phosphorous is a fundamental element for all living organisms as an important part of nucleic acids and for energy transference processes. It is intensely used by humans for fertilizers and detergents (Quevedo and Paganini 2011). It is also a limiting factor of crop production, since it is necessary for plant growth. The molar proportion demanded by ecosystems for biomass production is 106:16:1 or 41:7:1 (C:N:P) in a mass base (Redfield ratio); however, most of the time there is excess phosphorus present in domestic and urban wastewater (Kadlec and Wallace 2009).

In domestic wastewater, phosphorous is present in the form of organic compounds such as proteins, and in mineral compounds, mostly as polyphosphates and orthophosphates, which originate from synthesized products, for example detergents (Quevedo and Paganini 2011). According to Metcalf and Eddy (2016), typical concentrations of P in urban wastewater range between 3.7 and 11 mg l^{-1}, and the average Total P value discharged per person ranges from 0.6 to 1 g day^{-1}.

In natural wetlands and streams, phosphorous is present in the form of dissolved inorganic P, dissolved organic P, particulate organic P and particulate inorganic P. Dissolved inorganic P is considered available for living organisms, and free orthophosphate is the only form of phosphorous that can be used by algae and macrophytes. However, linearly and cyclical-structured condensable polyphosphates are also present. In addition, phosphorous bound to organic molecules is present in organic phospholipids, nucleic acids, nucleoproteins, phosphorylated sugars or condensable organic polyphosphates. Organic P, however, must be transformed into inorganic P in order to become available for organisms (Reddy et al. 1999; Vymazal 1995).

Theregowda et al. (2019) verified by emergetic accounting that nutrient recovery from wastewater is a sustainable and promising alternative for the management of sectors that connect water, nutrients and food production. Recirculating urban wastewater for agriculture is an opportunity to recover phosphorous (Cordell 2008).

According to Roy (2016), composting, vermicomposting, biogas products, P accumulation by plants, algae and trees, phytoextraction, zooextraction, aquaculture, aquaponics and hydroponics, filtering substrates, urine and human feces are also considered in the opportunities field for recovery and recycling of P through the concept of ecological engineering.

Phosphorus removal from effluents contributes to the reduction of the water footprint, so that effluent treatment plants have a positive action on the urban water cycle and protect waters from untreated discharge. Comparing systems without treatment, secondary treatment and treatment with phosphorus chemicals, results in a reduction in water footprint of 51.5% and 72.4% in the last two scenarios, respectively (Morera et al. 2016).

The concept of circular economy has become essential nowadays; therefore, it is necessary to rethink the recovering of nutrients in order to close the cycle loop. Both natural and modified sorption materials can present satisfactory efficiencies, especially when treating wastewater from constructed wetlands (Kasprzyk and Gajewska 2019). To make this feasible, it is mandatory to break the aversion that exists in relation to human excreta, which makes it difficult for producers and professional to realize the value of this resource, and enable the sanitation and food production sectors to cooperate and work together (Cordell 2008).

It is important that technologies be developed to recover phosphorous and close its cycle in order to implement a circular economy that can ensure sustainable development. The use of reactive waste materials in WCs allows the recovery of these nutrients and the quality of effluents emitted in a way that does not alter the natural patterns of the recipient body and so create a closed cycle, minimizing the waste of this resource (Fig. 1).

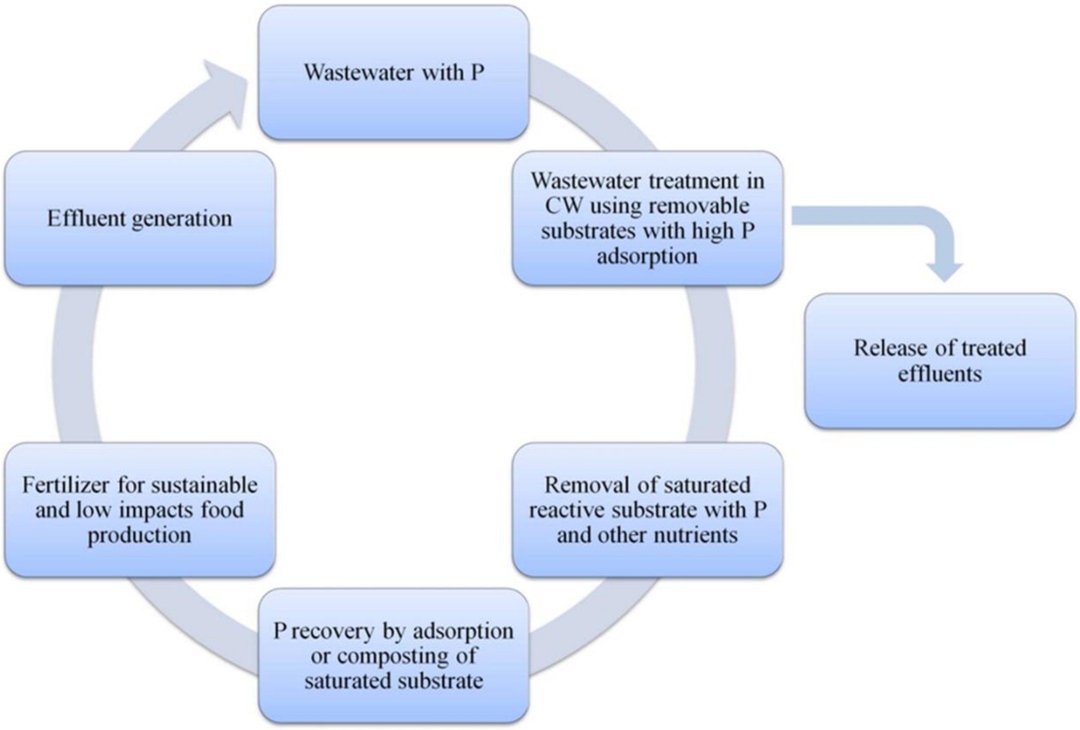


Fig. 1 Closed loop of circular cycle of P integrating the treatment of wastewater and food production. Source: adapted from Bunce (2018), Kasprzyk and Gajewska (2019).

Regarding the management and design of new wastewater treatment plants and water treatment plants, it is recommended to plan the future increase in quality of clean water as well as the recovery of resources and energy (Metcalf and Eddy 2016). In this context, the CW, an ecological engineering alternative, is a sustainable approach to recovering phosphorous from wastewater, while decreasing pollution of aquatic ecosystems, better local aesthetics, providing opportunities for food production and leisure opportunities (Peng et al. 2018).

3.2 Bibliometric Analysis

3.2.1 Current Scenario of publications related to Phosphorous Removal in Constructed Wetlands

From the using as the search terms: "*Phosphorus removal in Constructed Wetlands",* data registered by the Web of Science platform in the form "of articles, proceedings paper, reviews, editorial material, notes, book chapters and early access were obtained. From these, 98.7% of the papers were published in English, 0.5% in Spanish, 0.5% in Portuguese and 0.3% in Polish. In addition, it was possible to verify an increasing trend in the number of studies related to the removal of phosphorous in CWs as compared to earlier registers since the year 1995. However, an expressive increase was only confirmed in 2009 as presented in Fig. 2.

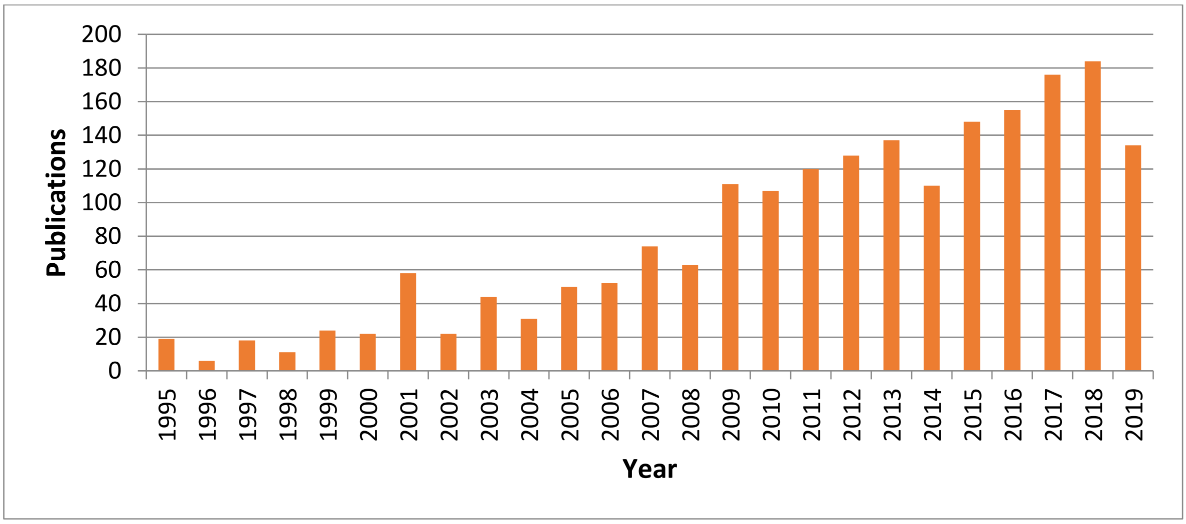


Fig. 2 Publications by year related to the search terms "*Phosphorus removal in Constructed Wetlands*" obtained though data from Web of Science.

It is worth mentioning that this research was performed in the second semester of 2019, and an increase is expected for the total number of publications in this year. Studies that specifically investigate phosphorous removal recently, since it is difficult to maintain efficiency for a long time according to conclusions by Colares et al. (2019), who obtained an average soluble P removal of 75% during the first eight months of operation; Later, the authors verified a significant reduction in removal efficiency.

Analysing the principle authors highlight Y.Q. Zhao with 46 publications; M. Scholz with 38 publications; U. Mander with 28 publications; H. Brix with 26 publications and J. Zhang with 22 publications. Figure 3 presents the top 25 authors with the most publications in this subject area.

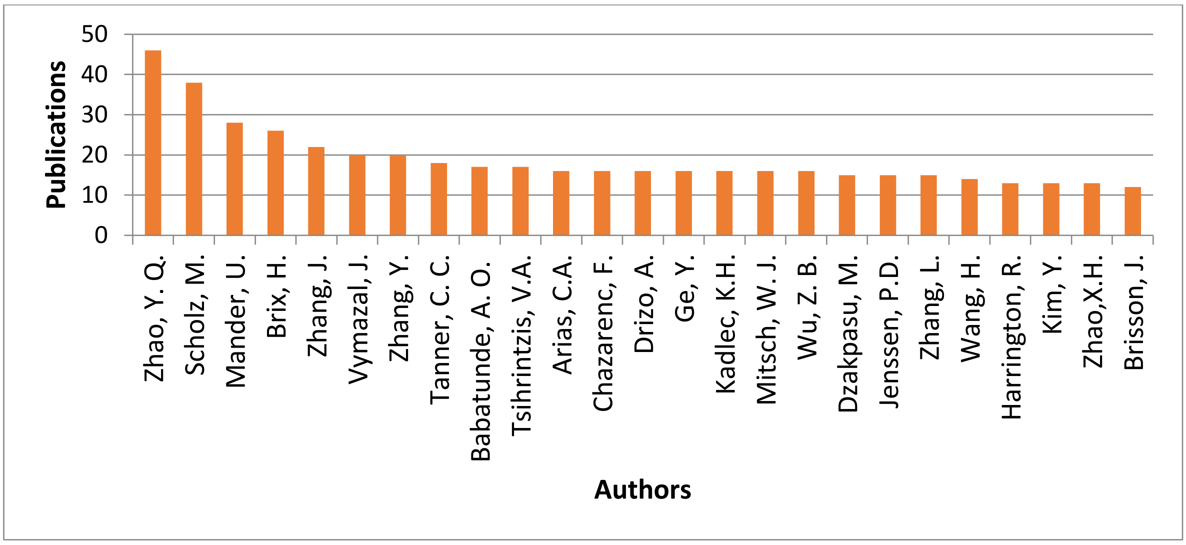


Fig. 3 Main authors related to search terms "*Phosphorus removal in Constructed Wetlands*", obtained though data from Web of Science.

In addition, the countries that published the most papers were China with 658 and the United States of America with 440 studies published from 1995 to 16 August 2019. Canada, Australia, Ireland, England, Sweden, France and South Korea each contributed over 50 published papers as shown in Fig. 4.

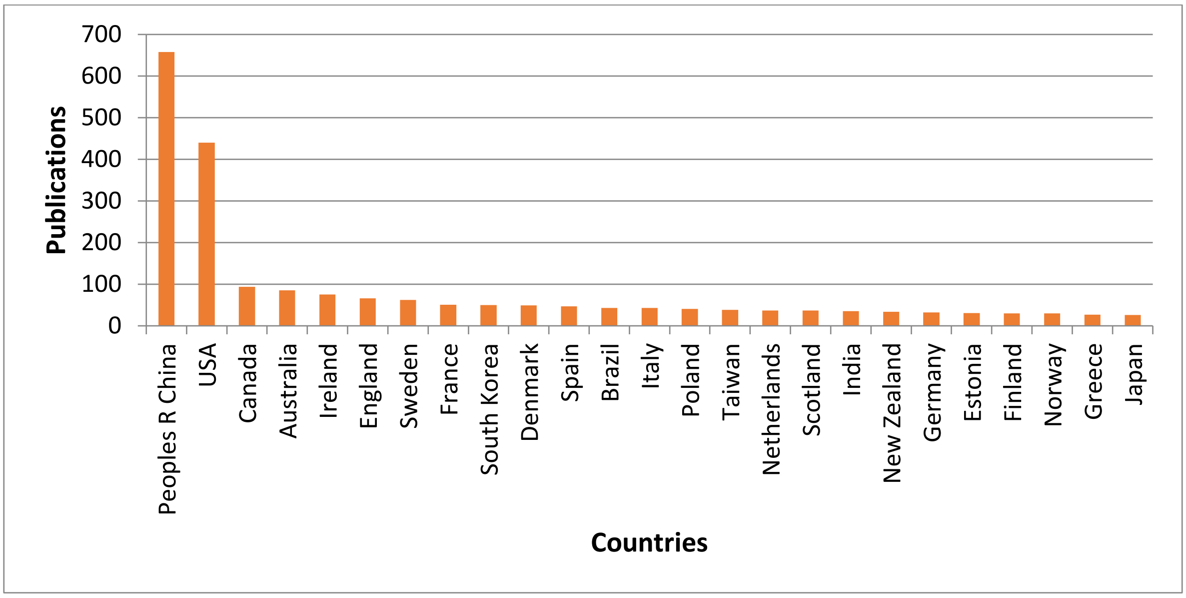


Fig. 4 Publication by country from 1995 to 16 august 2019 related to "*Removal of Phosphorus in Constructed Wetlands*", obtained though data from Web of Science.

3.2.2 Bibliometric mapping performed by searching for the terms "Phosphorous Removal in Constructed Wetlands"

Using the combination of words "*Phosphorus removal in Constructed Wetlands,*" data from titles, abstracts and key words in published papers found 2,020 results on the *Web of Science* platform for research conducted on 16 August 2019. The data were analysed using the software VOSviewer version 1.6.10, being extracted from the "Title and Abstracts" fields and applying binary counting with a minimum number of term occurrence of 10 times, and resulting in network visualization maps. In this type of visualization, items are presented as a label and a circle, and their sizes are determined by each ones importance. The lines between items present links, and the distance between two items in the visualization indicates the strength of their linking connection (Eck and Waltman 2019).

Fig. 5 shows the analysis of all terms extracted by VOSviewer on the map generated by the network view. Three large clusters were formed. The blue cluster focussed on factors related to the removal of other nutrients (nitrogen) and the presence of organic matter (chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total suspended solids), in addition to operational factors such as hydraulic retention time, hydraulic loading rate, flow type (horizontal, vertical and hybrid), effluent type, seasons and climate. The green cluster is related to biological factors, mainly involving plant species and biomass. The red cluster has been shown to be mainly linked to phosphorus removal factors involving substrate and physicochemical factors.

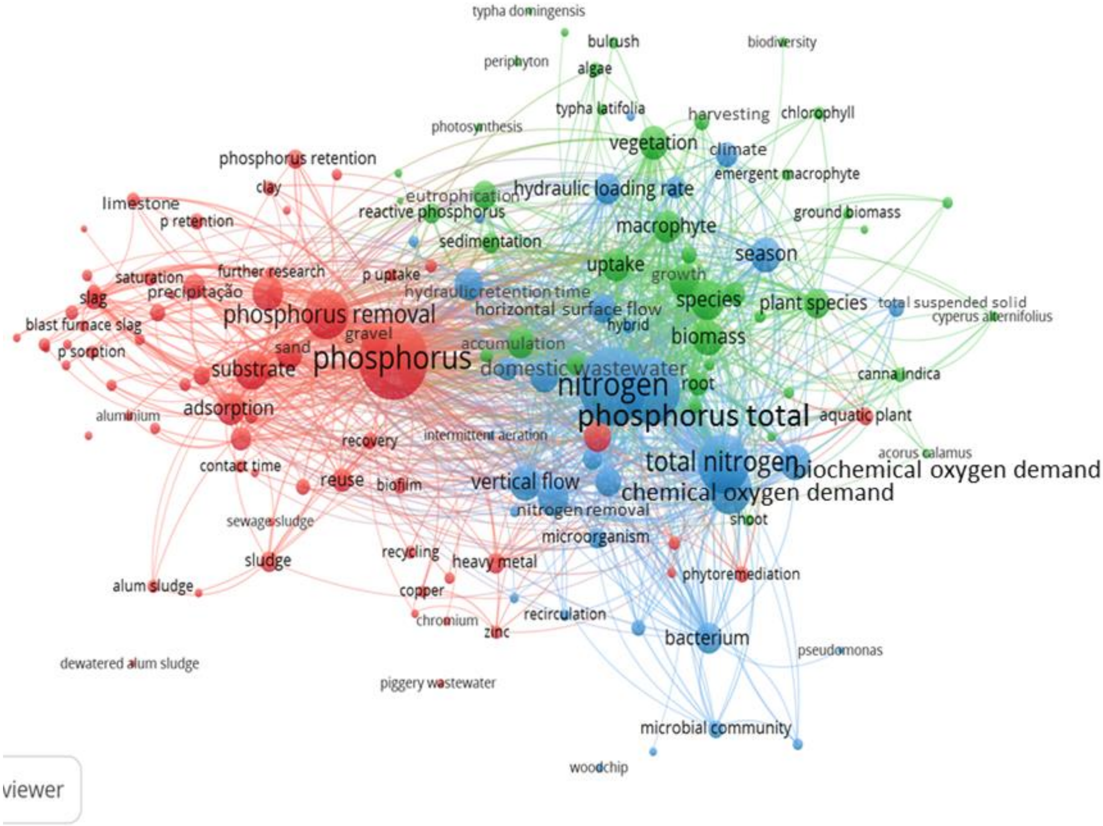


Fig. 5 Bibliometric Network Map generated in VOSviewer from the search terms "*Phosphorus removal in Constructed Wetlands*, using 2,020 results obtained though data from Web of Science.

Attention was drawn in Fig. 5 to the items total phosphorus, nitrogen, BOD, COD, phosphorus removal, substrate, adsorption, precipitation, gravel, season, species, vegetation, biomass, vertical flow, horizontal surface flow, domestic effluent, absorption, sedimentation, accumulation, hydraulic retention time, hydraulic loading rate, saturation, reuse, recovery, harvest, growth and roots. Phosphorous removal is also present with a strong connection to COD and BOD, which indicates that P may be associated with the organic matter entering a CW. Some emerging substrates (blast furnace slag, slag and limestone) and some plant species such as *Thypha dominigensis*, *Canna indica*, *Cyperus alternifolius*, *Thypha latifolia* and *Acorus calamus* also appeared.

The most important processes related to P immobilization are substrate adsorption, chemical precipitation, bacterial retention and absorption by plants and algae, incorporation into organic matter and sediment accumulation (Kadlec and Wallace 1996). This information is in accordance with the results presented in Fig. 5.

3.2.3Analysis of main items related to Phosphorous Removal in Constructed Wetlands

It is important to note that items of extreme importance may overlap. In this case, in order to have a better view of the items, a selection was made within VOSviewer of the most relevant terms and a new map was generated by the selection of terms with 60% or more relevance (defined by the software), thus generating a new visualisation as shown in Fig. 6.

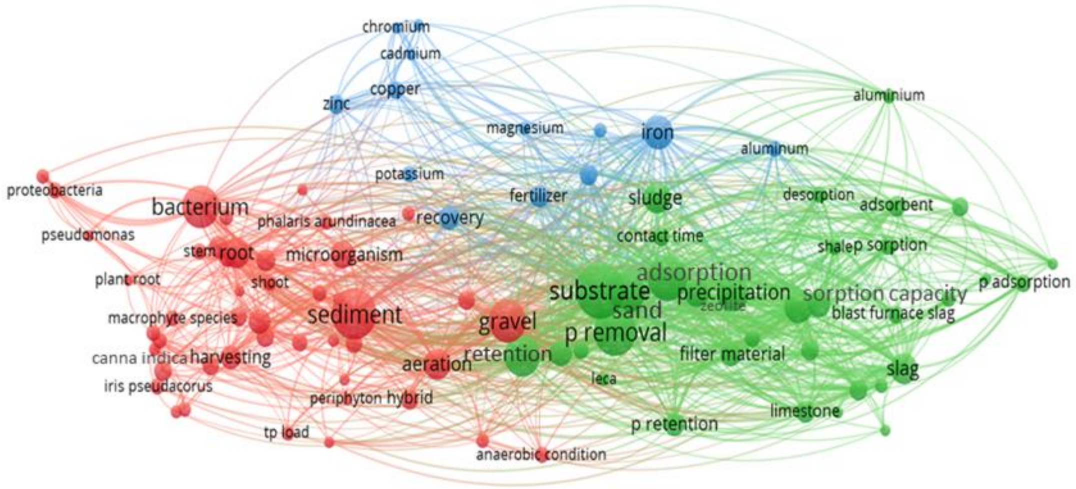


Fig. 6 Visualization of terms with 60% or more relevance selected within VOSviewer to avoid overlapping, obtained though data from Web of Science.

In the blue cluster presented in Fig. 6, it is possible to note that the main element connection of P is Iron (Fe), even though other elements were observed, such as Calcium (Ca), Magnesium (Mg) and Aluminium (Al). Other highlighted terms were contact time, aeration, bacterium, sediments, roots and plant biomass. In the green cluster, materials more recently applied as substrates: limestone, slag, shale, LECA (light expanded clay aggregate) and clay were present.

Material granulometry, specific area, contents of Fe, Al, Mg and Ca from substrates and the amount of organic matter can directly influence in P removal rates. Chemical precipitation in substrates containing Fe is more efficient than the ones containing Ca, and the addition of organic matter also impacts P adsorption, since it reduces pH in all treatments here researched (ceramics, zeolites, activated carbon, blast furnace slag and sand). Using slag as substrate in a treatment, the organic matter content increased from 0 to 16%, and the pH of the treating solution decreased from 12.23 to 8.86 (Dai and Hu 2017).

The bibliometric analysis from the current study presented some plant species such as *Pragmites australis, Canna indica, Typha latifólia* and *Cyperus papyrus.* Phosphorous removal may be enhanced by using CW vegetated with a single species or combining different plant species, for example *J. effusus* and *C. lúrida*; although removal efficiencies depend on the presence of plants and their species (Menon and Holland 2013).

Some plant species present higher capacities for P uptake and assimilation. Du et al. (2017) evaluated an Integrated Vertical Flow Constructed Wetland vegetated with *Arundo donax, Canna generalis, Typha orientalis* and a control system without plants. The authors found that the treatment system planted with *Canna x generalis* removed up to 77% of total P.

On the other hand, Fia et al. (2016) obtained average Total P removal of 78 ± 15% from an unplanted CW and 74 ± 17% removal efficiency from a CW using Taboa and 73.5 ± 15% in a CW vegetated with Tifton-85 bermuda grass (*Cynodon* sp.); all systems were filled with gravel. Not much difference was observed between planted and unplanted systems; the researchers even reported that the highest P removal may have occurred due to the fact that the systems were built shortly before the operation started thanks to the capacity of absorbing and precipitating compounds with elevated P contents due to higher pH values.

In general, macrophytes have lower capacity for absorbing P than N because, under anaerobic conditions, insoluble phosphates are precipitated by Fe, Ca and Al ions. Besides, phosphates can be adsorbed by organic peats, clay and by Fe and Al oxides. Likewise, it is important to mention that phosphorous can be linked to organic matter through assimilation of bacterium, algae and macrophytes (Kumar and Dutra 2019). Over the long term, P can be removed by plant harvesting and, when the sediments with P are removed from the system, the circular economy concept, in which nutrients can return to their source in a closed circuit (Ziegler 2016), is approached.

The absorption of phosphorous by plants is balanced by its release during tissue decomposition. Plants and microorganisms affect the chemical conditions of their surroundings and therefore influence P as well; and thus, pH changes can lead to P precipitation with $CaCO_3$. Sedimentation, molecular diffusion and mixture also affect the capacity of P assimilation by the system (Reddy et al. 1999).

Aeration was a term that also stood out during the bibliometric analysis. When comparing natural wetlands and constructed wetlands, it was verified that dissolved oxygen concentration in water influences P removal. The wetland which presents high oxygen concentration promotes the formation of Fe (OOH)n and the binding of P to its surface (Di Luca et al. 2017).

According to bibliographic study conducted by Ilyas and Masih (2018), CW with artificial aeration usually present higher treatment efficiencies than no aerated CW. In artificial aeration, the global efficiency of total P removal averages 68 ± 20%, and for the no aerated ones, it is 48 ± 23% with removal rates of 1.1 ± 1.4 and 0.4 ± 0.4 g m^{-2} day^{-1}, respectively.

The pH is another factor that influences phosphorus removal and also appears in the bibliometric research, and the reduction of P reached 71.5% in pH 5. With the increase in pH values between 5 and 7, and the absorption applied at 0.5 $mg.g^{-1}$ substrate, removal rates increased to 95.6% at pH 7. At pH 7 to 11, phosphorus removal rates increased slightly to 99.4% (Cheng et al. 2018). Oliveira et al. (2011) obtained the best P removal results in a pH range between 5.0 and 8.0.

In the selection of a specific item from the same map as Fig. 6, it is possible to note the connections between the most linked items. For example, when selecting the term "bacterium", the highlighted terms are substrate, pseudomonas, proteobacteria as shown in Fig. 7. These microbiological aspects have fundament roles in system performance, since the periphyton acts in the transformation of P in biologically available forms (Reddy et al. 1999).

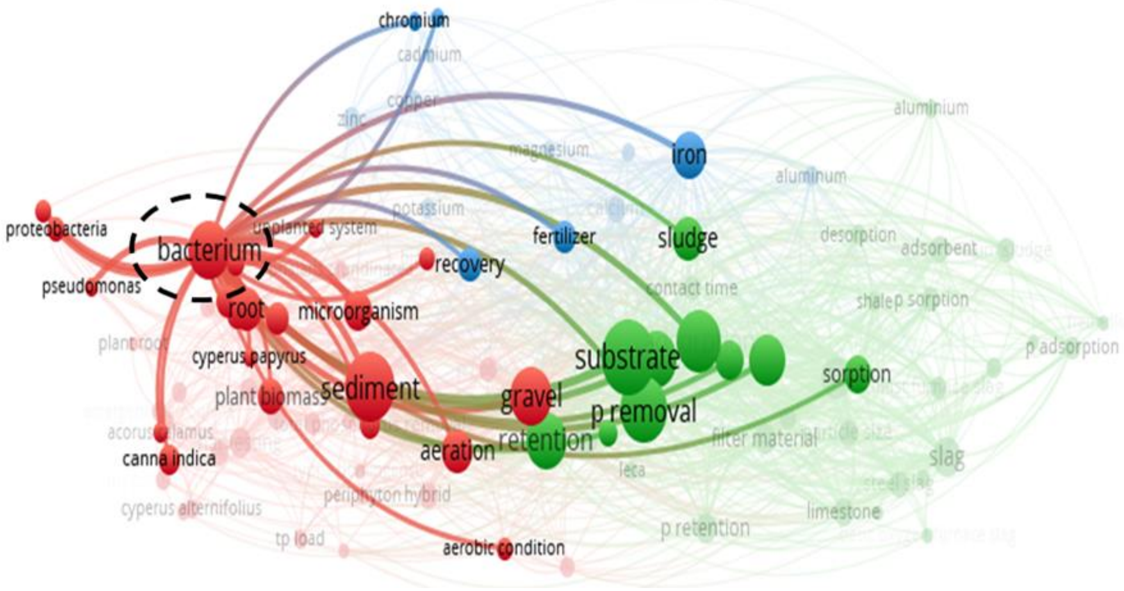


Fig. 7 Selection of highlighted terms related to the Bacterium item in Phosphorous removal in CWs, obtained though data from Web of Science.

The *Pseudomonas* genus may be the main actor in the aerobic biological adsorption of phosphorous in CWs with integrated vertical flow. Du et al. (2017) found a significant correlation between the poliphosphate quinase activities and the *Pseodomonas* frequency ($R^2 = 0.554$).

The main bacterium found in a CW filled with pyrite, which presented average P removal of 87.7 ± 14.2%, were *Anaeromyxobacter* (4.9%), *Ramlibacter* (4.8%), *Defluviicoccus* (4.2%), *Azoarcus* (3.7%) and *Geobacter* (3.4%) and were highly related to anaerobic and aerobic pyrite oxidation. Removal efficiencies for total nitrogen (TN) were higher during summer and autumn, and lower during winter in CWs. On the other hand, P removals were steady during the different seasons (Ge et al. 2019), this aspect indicates that P removal depends more on physical-chemical phenomena than on biological aspects.

When the "*P removal*" term was selected, its connection with substrate, precipitation, adsorption, sorption, P concentration, gravel, sand and retention became clear, and it was possible to observe the item "roots" standing out in relation to leaf and stems, and also highlighting "plant biomass" as shown in Fig. 8.

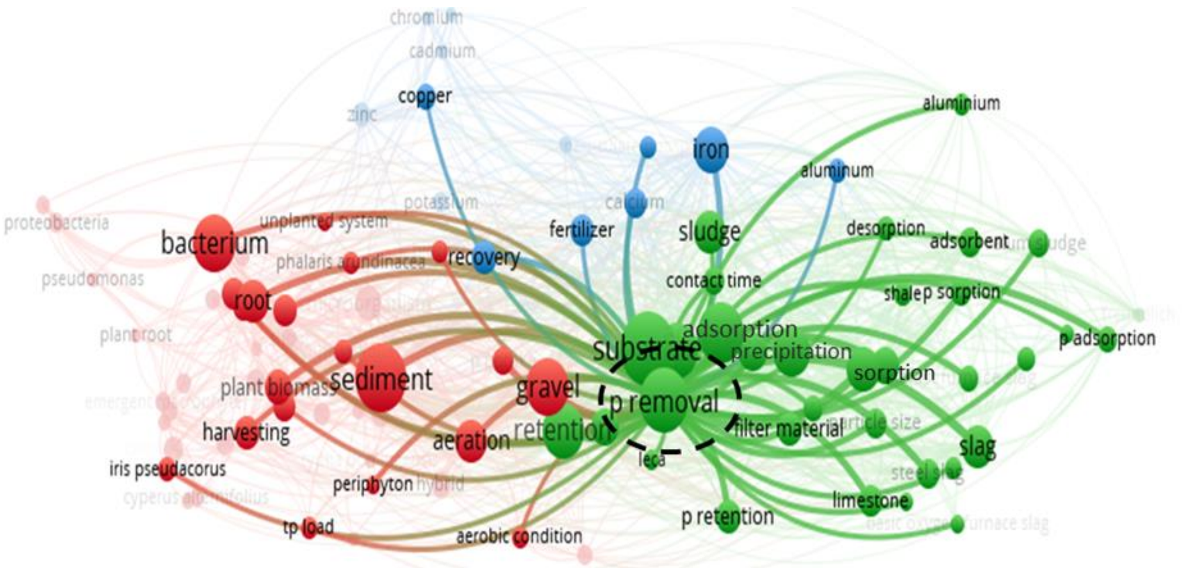


Fig. 8 Selection of highlighted terms related to phosphorous removal, obtained though data from Web of Science.

When selecting the "P removal" item in Figure 8, a clear visualization of the items was observed; again, the highlighted terms were "substrate," "adsorption," "sediment," "retention" and "precipitation." The terms gravel and sand, stood out due to the fact that they are the most applied substrates today.

Biomass production, presented in Fig. 9, also indicates the importance of regular harvesting of plants and system maintenance, by removing sheets and other decomposing tissues so that the removed nutrients are not released back to the CW treatment water.

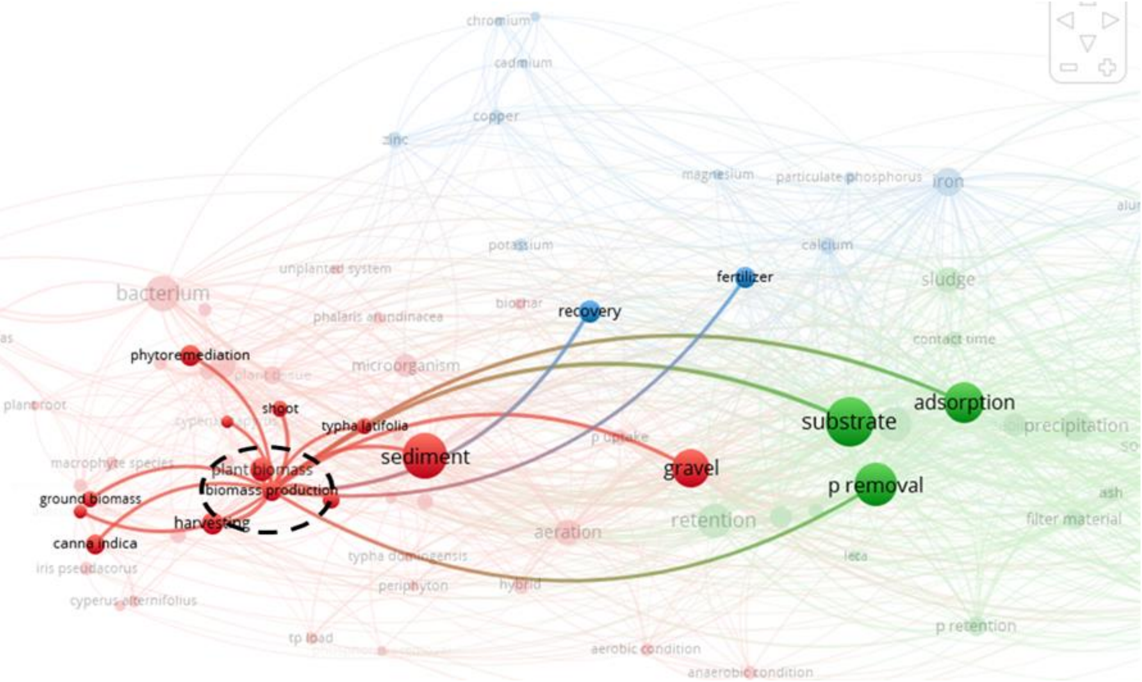


Fig. 9 Selection of highlighted terms related to biomass production, obtained though data from Web of Science.

For total P removal, the species *Salix babylonica, Gypsophila* sp and *Oenanthe javanica* were the most recommended by Zhu et al. (2011), who obtained removal rates of 0.331 g m^{-2}, 0.247 g m^{-2}and 0.167 g m^{-2} of total phosphorous, respectively. The authors did not verify a consistent and regular pattern concerning N and P distribution in leaf, stems and roots.

Haritash et al. (2017) verified that P concentration in *Canna lily* before treatment ranged from 0.1–1.3 mg P g^{-1} in leaf, from 1.7 to 4.2 mg P g^{-1}, 1.7—2.8 mg P g^{-1} in plant roots and from 4.4 to 5.1 mg P g^{-1} in stems; thus recommending regular pruning of plant tissue above ground to improve nutrient removal from the system.

The growth rate and development phase of plants are related to nutrient removal. The *Typha domingensis* macrophyte removed 5.12% and 3.16% of N and P loads, respectively in a Horizontal Flow CW. The highest removal efficiencies were verified during the period of greatest leaf growth (Pelissari et al. 2019).

Additionally, Campos and Teixeira Filho (2019) obtained evidence that during early plant (*E. crassipes*) development, more nutrients are demanded than during the maturation phase. In this sense, Pelissari et al. (2019) strongly recommends that plant harvesting is always performed when they reach their maximum growth. For example, for *Typha domingensis Pers*, between 60 and 90 days after pruning.

The bibliometric mapping supports the conclusions from Machado et al. (2017) that the substrate is one of the most important factors that influence pharmaceuticals, personal hygiene products and phosphorous, and the most used materials in Brazil are gravel, sand, the mixture of both materials and steel slag. The main mechanism for phosphorous removal is chemical precipitation resulting from the association with calcium, aluminium and ferrous ions present in those materials.

Due to the fact that the substrate is the main factor involved in phosphorus removal processes in CWs, a new figure was made selecting only the items related to the types of materials used to fill the WC as shown in Fig. 10.

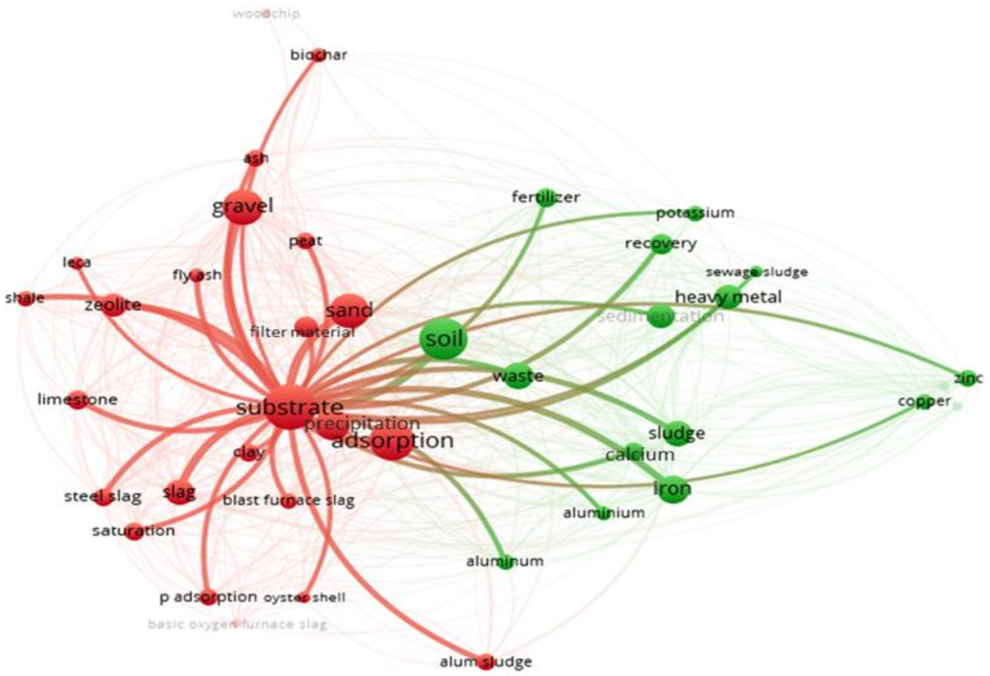


Fig. 10 Selection of highlighted terms related to the substrate, obtained though data from Web of Science.

In Figure 10, heavy metals are attached to the substrate. Among the most used are gravel and sand followed by soil, waste, biochar, peat, fly ash, zeolite, LECA, limestone, shale, steel slag, clay and sludge. Among the chemical elements, iron and calcium stand out.

The low occurrence of research applying to ceramics as substrates may justify the absence of this term in the bibliometric mapping. In Brazil, however, research such as that of Lima et al. (2008) obtained promising results regarding the application of broken bricks as substrate material in Constructed Wetlands.

Therefore, the role of the substrate and how its saturation affects phosphorous removal is clear according to research such as that performed by Colares et al. (2019), who obtained average P removal of 93.6% during the first operation trimester, and later, observed a decrease to 29.6% removal over three months of monitoring. In addition, the authors also noticed that in the Hybrid CW system, the unit that contained substrate (gravel) was more efficient in removing P than the ones without substrate (floating treatment wetlands).

Thus, the substrate is an important aspect of constructed wetlands, providing support for vegetation, filtering, water draining, superficial areas for biofilm fixation and biofilm growth, as well as treatment by adsorption and transformation processes (Tsihrintzis 2017).

It is fundamental to consider several factors when evaluating the viability of an application of a material as substrate. Ballantine and Tanner (2010) conducted an analysis evaluating substrates using a score on a scale from 0 to 10 for efficiency in removing P, estimated cost, availability (in New Zealand) and recovery/reuse potential. The analysed materials that presented the highest scores (≥ 8) were: allophane, tephra (P), limestone, shale, Filtralite, LECA, Phoslock^{TM}, slag and tree bark.

Among the most used materials, the most popular are natural ones, with removal of up to 40 g P kg $^{-1}$ for heated Opoka for example. Industrial materials have removals of up to 420 g P kg^{-1} for some steel slags and for artificial filters, such as Filtralite, which can remove up to 12 g P kg $^{-1}$ in a process under pH> 7 and with high Ca content (Vohla et al. 2011).

Yang et al. (2018) have classified substrates according to the main pollutant removal mechanisms in CWs, such as ion exchange capacity, P sorption capacity and electron donating capacity. The search for new substrates is encouraged with the aim of increasing P removal efficiency.

Wu et al. (2019) found P removal ranging from 87.1 to 91.9% in Vertical Flow CW using different layers of bioceramics, zeolites and anthracite, and vegetated with *Canna indica L.*

According to Cessa et al. (2009), material porosity directly influences the superficial area of solids and amorphous materials as well as Fe and Al oxides from the clay fractions extracted from soil were significant with respect to P adsorption. Tuyan et al. (2018) found a superficial area of 5.570 cm^{2} g^{-1} for brick residues with dimensions ranging from 10 µm to 100 µm.

The materials that contain clay present potential for removing phosphorous from CW and at the same time the advantage of reusing the material as fertilizer since it slowly desorbs the retained P over time. The increase in the superficial area of clay also significantly increases P sorption, so that fine calcined clay (0.25–

0.85 mm) presents higher removal capacity than coarse calcined clay (0.8–4.75 mm) and bricks (0.8–4.57 mm) (White et al. 2011).

In a CW system filled with bricks and clay and vegetated with *E. crassipes*, P removal efficiencies of 82% were obtained; 87% with unplanted systems. It was observed that after 296 days of operation, there was no desorption or P increase in the effluent. This may indicate an elevated affinity between P and the substrate, and thus the adsorption processes in the present system is higher (Lima et al. 2018).

A research using calcium-rich attapulgite which was heat treated, and presenting several particles sizes (0.2–0.5 mm, 0.5–1 mm and 1–2 mm) in a column treating synthetic wastewater in batch flow, were found removal efficiencies higher than 95% for P in less than an hour and a maximum sorption capacity ranging from 4.46 to 5.99 mg P g^{-1}. The authors also observed that particles sizes were proportional to removal capacity, and that P sorption mainly occurred by calcium precipitation present in attapulgite (Yin et al. 2017).

Both calcined clay and clay brick present high phosphorous retention capacities, and after analysis of adsorption and desorption, average retentions found for phosphorous were 95.7 mg kg^{-1} for bricks, 495 mg kg^{-1} for coarse calcined clay and 1,230 mg kg^{-1} for fine calcined clay (White et al. 2011).

In a study performed using coal flying ash, water sludge and oyster shell, in a ratio considered ideal of 6:4:0.8, and subjected to heat treatments at a temperature of 1050ºC, a maximum phosphorous adsorption of 4.51 mg g^{-1} was obtained. Active calcium was the most influential component because neutral-alkaline conditions facilitate the formation and precipitation of calcium phosphates. Material with active components such as Ca^{2+}, Fe^{3+} and Al^{3+}can promote phosphorous adsorption sites (Cheng et al. 2018).

In laboratory experiments (bench scale) using active barriers comprised of aluminium oxides immobilized in polyolefins to remove phosphorous from water, removal values of around 11.1 µg cm^{-2} were obtained, removing more than 90% of phosphorous from a solution containing 100 µg L^{-1} in batch flow experiments conducted for 90 days (Oliveira et al. 2011).

Kasprzyk and Gajewska (2019), when applying residual materials which were heat treated in temperatures over 700 °C, and comprised of carbonate-silicon rock and lanthanum-modified bentonite (artificial source), found sorption capacities for phosphates of 45.6 mg g^{-1} and 5.6 mg g^{-1}, respectively.

In a study performed with horizontal subsuperficial flow CW using natural pyrite and limestone as substrate, average removal of 87.7 ± 14.2% for TP and 69.4 ± 21.4% for total nitrogen were obtained. The main form of P found in CW with pyrite was within the Fe and Al elements (Ge et al. 2019).

Cui et al. (2008) found maximum sorption capacities of substrates of 4243 mg kg^{-1} for turf, 2116 mg kg^{-1} for blast furnace artificial slag, 1598 mg kg^{-1} for blast furnace slag, 1449 mg kg^{-1} for artificial coal burning slag, 1369 mg kg^{-1} for superficial soil, 194 mg kg^{-1} for coal burning slag, 519 mg kg^{-1} for artificial sand, 494 mg kg^{-1} for gravel and 403 mg kg^{-1} for medium-sized sand.

Heat treatments can contribute to increased P removal. For example, a removal efficiency of 6.94 mg g^{-1} was obtained for heat-treated bentonite (800 °C), while for the treated bentonite under 400 °C, a removal efficiency of 0.483 mg/g was obtained and untreated bentonite (in its natural form) only reached 0.237 mg g^{-1}. The bentonite treated at 800 °C rapidly removed 94% of P from a solution containing 10 mg of P L^{1}, and thus it can be concluded that the main factors affecting phosphorous adsorption capacity were the changing of the crystalline structure combined with the strong calcium release capacity and even higher stability under different pH conditions (Chen et al. 2018).

Table 1 presents extracted data from a performed review using several technologies applied for P removal and under different CW configurations.

Table 1 Selection of some materials used in the last three years by various authors

Material/Technology applied in CW	P removal efficiency	Sorption capacity	Plant species	CW conifguration	Reference
Calcium-rich attapulgite after heat treatment and in different size particles	93.1% - 95.4% Average removal of phosphates over 150 days	4.5 -5.9 mg P g^{-1}	-	Vertical columns	Yin et al. 2017.
Magnesia and magnesite added to gravel and sand substrate	93.3 e 75.8% Total P removal average	-	*Phragmites australis*	CW Microcosms, built in polyethylene drums	Lan et al. 2018.
Steel slag + biochar -Microelectrolysis Fe/C	93.6 ± 5.3% Total P removal average	-	*Iris tectorum Maxim*	Subsuperficial CW intensified with micro-electrolisys	Shen et al. 2019
Natural pyrite	87.7 ± 14.2% Total P removal average	8.5 mg P g^{-1} in the substrate from inflow zone	*Juncos comuns (P. australis)*	CW horizontal flow	Ge et al. 2019
Photovoltaic Electrolysis and Filling with Graded Stones, Soil and Rice Straw Biochar	67.6% Average removal for phosphates	-	*Hydrocotyle verticillata; Iris germanica; Potamogewton crispus; Myriophyllum verticillatum and Hydrilla verticillate*	CW horizontal Flow combined ith electrolysis and CW FreeWater Surface	Gao et al. 2019
Activated alumina	96.4% Total P removal average	-	-	Bench scale	Tan et al. 2019
Gravel;	98.0 ± 3%	-	*Iris pseudoacorus*	CW vertical flow	Shi et al. 2017
Red bricks;	99.0 ± 2%	2.3 mg g^{-1}			
Fly ash from bricks.	100.0 ± 0.3%	5.2 mg g^{-1}			

Table 1 Selection of some materials used in the last three years by various authors

Material/Technology applied in CW	P removal efficiency	Sorption capacity	Plant species	CW conifguration	Reference
*Both with aeration rates of 1.0 L.min^{-1}	Total P average removal				
Sustainable Ceramic from coal fly ash/ sludge/ oyster shells	99.4% and pH 7–11	4.5 mg g^{-1}	-	Performed in a glass column	Cheng et al. 2018
	Total P removal average				
Wheat straw	66.8%	-			
Apricot lump	66.4%		*Iris pseudacorus*	Subsuperficial flow with intermittent aeration of 0,8 L.min^{-1} over 4 h/day	Wang et al. 2019
Nut shell	80.3%				
	Average removal for wastewater containing 6 mg L^{-1}				
Palm kernel shell	42.5%	-	*Thalia geniculata and Typha latifolia*	CW horizontal flow (Pilot Scale)	Okoye et al. 2018.
	Average PO_4 removal				
Biochar from:					
Corn cobs;	71.0 ± 1.0%	2.2 ± 0.2	-	CW vertical flow	Kizito et al. 2017
Wood;	83.0 ± 4.0%	3.3 ± 0.6			
	Highest averages for total P removals	Maximum value in mg/g de PO_4 3.6 mg P g^{-1} (pH 5)			
Fast Cooling Furnace Slag	73.7% of phosphate removal (200 mg l^{-1}) by applying a dose of 5 g of adsorbent	> 2.5 mg P g^{-1} (pH 7)	*Iris pseudoacorus*	CW horizontal flow	Park et al. 2017
		> 1.46 mg P g^{-1} (pH 9)			

Generally, most technologies investigate aspects regarding electrochemical, physisorption, chemisorption or the formation of bacterium biofilms.

In order to improve P removal in a CW, it is possible to add a separate porous filter unit with an easily removable material with high sorption capacity. In addition, the materials to be applied as substrates in CW must present moderate to high affinity with P, be renewable and natural, abundant, available at low cost, nontoxic, capable of later reuse without modifying the quality of the soil or the water over short and long terms (Ballantine and Tanner 2010). In addition, saturation time, heavy metals presence, recyclability of filtering medias as fertilizers and hydraulic loading must be considered when selecting the filtering material (Vohla et al. 2011).

Another important aspect is that recycling residues as filter substrates can significantly reduce the cost of building CW, and reduce the volume and add economic value to waste (Yang et al. 2018). In the bibliometric mapping, the item "recovery" stood out (Fig. 11). It linked to terms related to phosphorous removal in CW and fertilizers, thus corroborating the idea that reuse of the reactive substrates after saturation can contribute to the recovery of this resource for agricultural production.

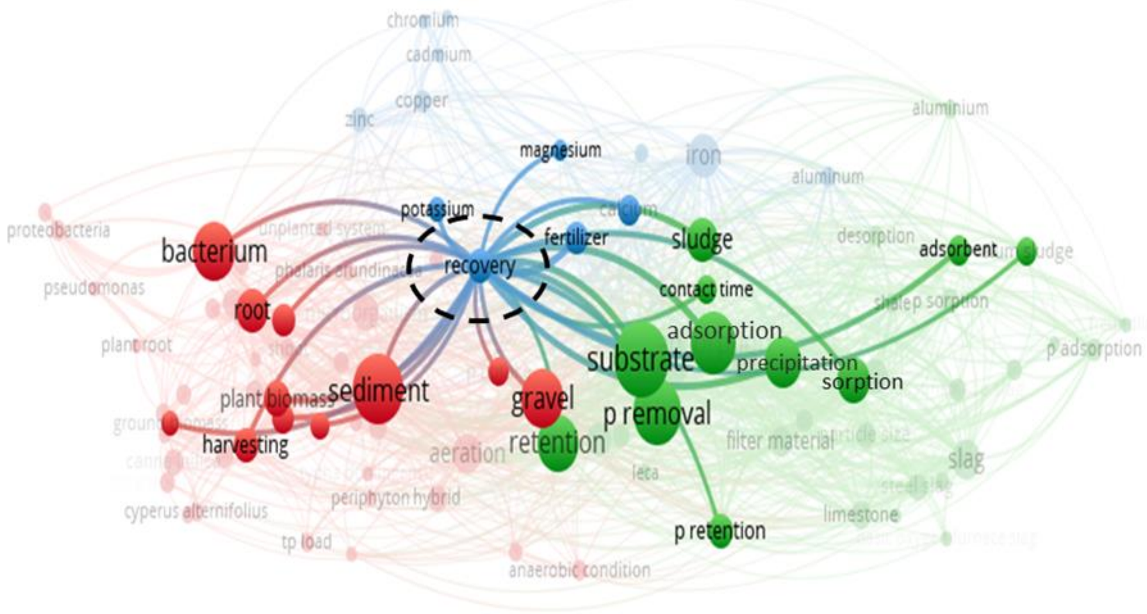


Fig. 11 Selection of the recovery item in the bibliometric map from the VOSviewer software, obtained though data from Web of Science.

In Fig. 11, the term recovery is presented as linked to the following items: substrate, phosphorous removal, sediment, bacterium, retention, adsorption, precipitation, sorption capacity, roots, harvesting and plant biomass, thus indicating possible ways for future research on minimizing waste and better management of this resource.

As observed in the bibliometric mapping, several factors can influence P removal in a CW, and the percentage of contribution from each of the factors is highly variable, and each one has an important role to play in the process, such as P transformation into more biodegradable forms (performed by microorganisms), P uptake and assimilation by plants in their biomass or adsorption in the substrate. In addition to the selected macrophyte species, it is important to investigate the role of substrates in consideration of the development of new material with higher removal capacities and with recovery possibility.

4 Conclusions

Food production and wastewater treatments should work together in order to supply population's demand for both food and good quality water. In this context, CW are a promising technology that approaches the circular economy concerning decentralised wastewater treatment. There are several mechanisms that influence phosphorous removal in a CW. These include the action of reactive substrates, microorganisms to generate bioavailable forms, incorporation into biomass, appropriate pruning frequency for their removal from the CW system, maintenance to prevent residual tissues from re-entering the system, as well as monitoring pH, dissolved oxygen, retention time and hydraulic load parameters.

On the other hand, the selection of an adequate substrate is by far the most determinant factor for enhancing this process. In addition, this supports the possibility of recovering this important element while preserving the environmental quality of water bodies, thereby becoming extremely beneficial, contributing to a more sustainable development concerning water management.

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5 CONSIDERAÇÕES FINAIS

A bibliometria e pesquisa bibliográfica foram ferramentas benéficas ao embasamento teórico para o desenvolvimento da parte prática do trabalho. Através do mapeamento bibliométrico foi possível identificar principais pontos a serem desenvolvidos e principais avanços na área de WCs e seus substratos com vistas a aumentar a remoção de nutrientes.

Pode-se observar que o principal mecanismo de remoção de P em WCs é físico-químico, sendo que deve-se observar principalmente a composição química do material, área superficial e disponibilidade local ao escolher o substrato.

Há uma grande variedade de substratos com potencial para serem utilizados em WCs com objetivo de remover Fósforo, tanto materiais residuais, naturais ou artificiais. É importante que esta escolha seja feita levando em consideração os princípios da economia circular.

Estudos futuros devem priorizar também a busca por alternativas para a recuperação de nutrientes através do substrato saturado de WCs, o qual deixaria de ser um resíduo após o tempo de uso.

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ANEXO I – PUBLICAÇÃO REVISTA REMOA - UFSM

REMOA/UFSM
Revista Monografias Ambientais

UFSM

Rev. Monogr. Ambient.
Santa Maria v.18, e1, p. 01-10, 2019
DOI:10.5902/2236130835929 - ISSN 2236-1308

Problemas Ambientais Submissão: 22/01/2019 Aprovação: 12/03/2019 Publicação: 26/07/2019

Artigo Original

Avaliação do Ciclo de Vida de sistemas de tratamento de efluentes urbanos utilizando Microalgas e Wetlands Construídos

Life Cycle assessment of urban effluent treatment systems using Microalgae and Constructed Wetlands

Naira Dell'Osbel[I], Ênio Leandro Machado[II]

Resumo

Desenvolver o saneamento de águas residuárias de forma descentralizada significa pesquisar a carência de quase 50% dos municípios brasileiros. Neste sentido a principal finalidade deste estudo foi o uso da Avaliação do Ciclo de Vida para aplicação dos sistemas integrados de reator anaeróbio, Wetlands Construídos (WCs) de fluxo vertical/horizontal e Microalgas (MA). A unidade funcional foi definida como 1.200 m3 de efluente tratado durante 20 anos e a fronteira do sistema foi delimitada pela entrada do esgoto bruto no reator UASB até a partida do efluente final tratado para o corpo receptor. O estudo de ACV utilizou o programa SimaPro® 8.04 e o método Impact 2002+. Para as categorias de impacto nas etapas de construção e operação foram aplicados a Normalização, Caracterização, Ponderação e Inventário de Rede dos dados obtidos. Desta forma foi possível a identificação dos principais itens para o desenvolvimento ambiental sustentável destes sistemas, sendo que foram identificados os maiores impactos na fase de construção (92,3%) relacionados a utilização de polietileno de alta densidade (32,8%), areia (27,2%) e policloreto de vinila (18,8%). Já na fase de operação o maior impacto foi a utilização de energia elétrica no sistema Microalgas Pré-Wetlands devido a dependência de recursos não renováveis.

Palavras-chave: Avaliação do ciclo de vida; Efluente doméstico; Wetlands construídos; Microalgas

Abstract

Developing wastewater sanitation in a decentralized way makes it possible to study the shortage of almost 50% of Brazilian municipalities. Thus, the main purpose of this study was the use of the Life Cycle Assessment for the application of the integrated systems of anaerobic reactor, Wetlands Constructed (WCs) of vertical/horizontal flow and Microalgas (MA). The functional unit was defined as 1,200 m3 of effluent treated for 20 years, and the boundary of the system was delimited by the entry of the raw sewage into the UASB reactor until the departure of the final effluent treated to the receiving body. The ACV study used the SimaPro® 8.04 program and the Impact 2002+ method. For the categories of impact in the construction and operation stages were applied the Normalization, Characterization, Weighting and Network Inventory of the obtained data. Through it was possible to identify the main items for the sustainable environmental development of these systems, with the highest impacts in the construction phase (92.3%) related to the use of high density polyethylene (32.8%), sand (27.2%) and polyvinyl chloride (18.8%). Already in the operation phase the greatest impact was the use of electricity in the Microalgas Pre-Wetlands system due to the dependence of non-renewable resources.

Keywords: Life cycle assessment; Domestic effluent; Contructed wetlands; Microalgae

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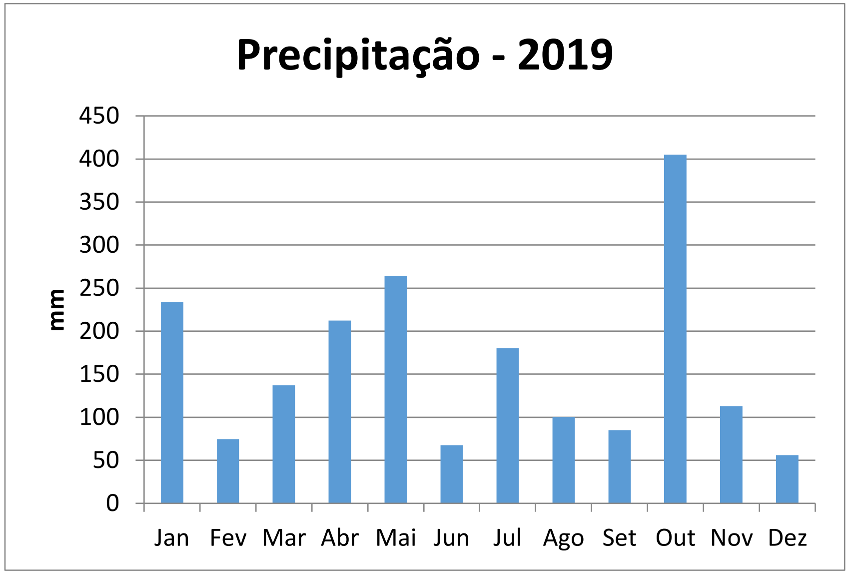
[I] Engenheira Ambiental, Mestranda em Tecnologia Ambiental pela UNISC, Universidade de Santa Cruz do Sul, RS, Brasil. enioleandromachado@gmail.com
[II] Químico Industrial, Doutor em Engenharia, Universidade de Santa Cruz do Sul, RS, Brasil. enio@unisc.br

ANEXO II – VARIÁVEIS CLIMÁTICAS REGISTRADAS NO PERÍODO DE MONITORAMENTO DOS SISTEMAS.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350
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250
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150
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50
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Mai
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Jul
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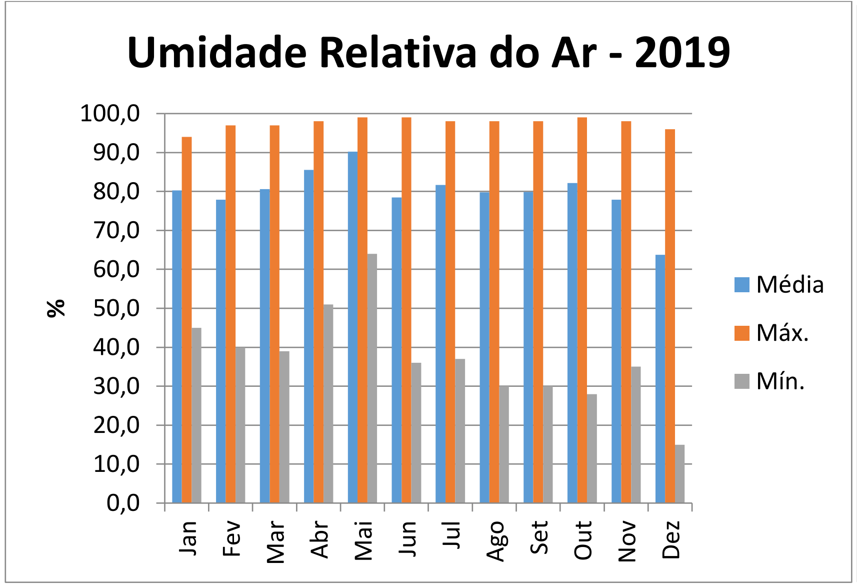
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50,0
40,0
30,0
20,0
10,0
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Jan
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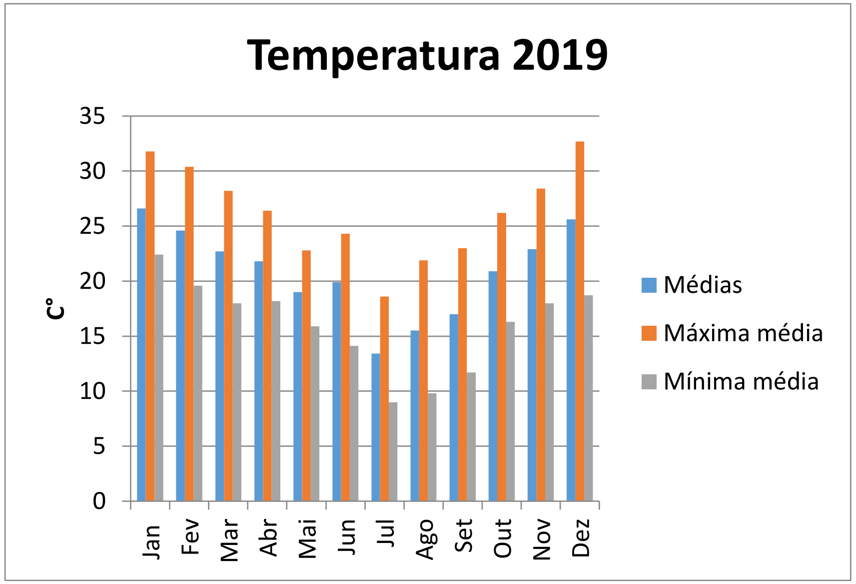
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25
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10
5
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Abr
Mai
Jun
Jul
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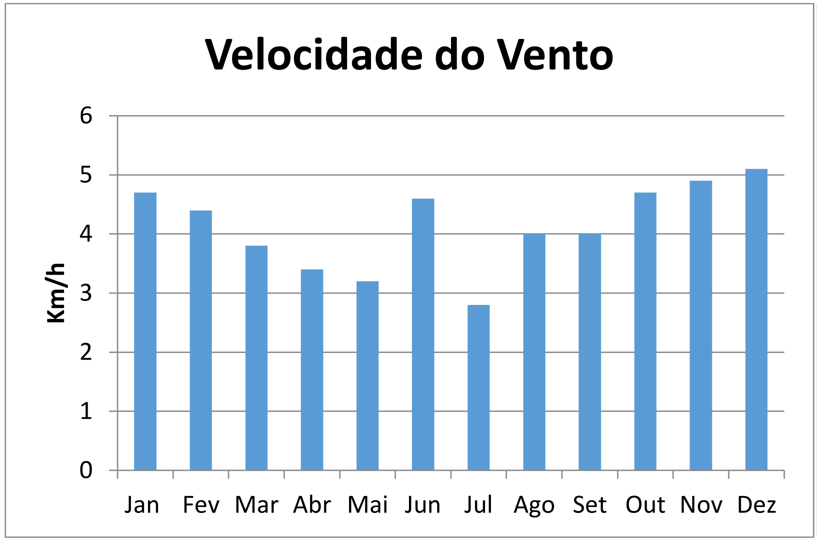
Out
Nov
Dez
Médias
Máxima média
Mínima média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Km/h
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4
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Fev
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Abr
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Nov
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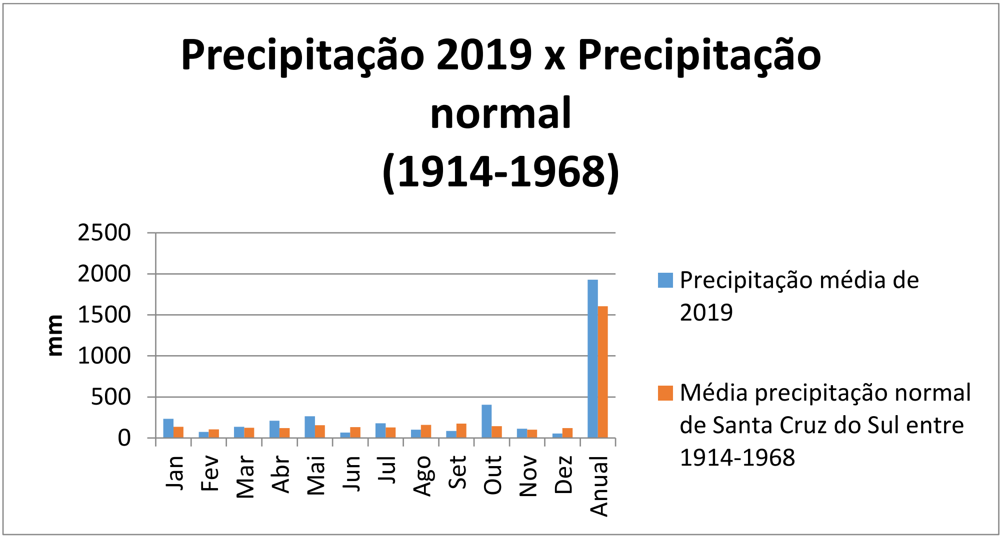
Precipitação 2019 x Precipitação normal (1914-1968)
mm
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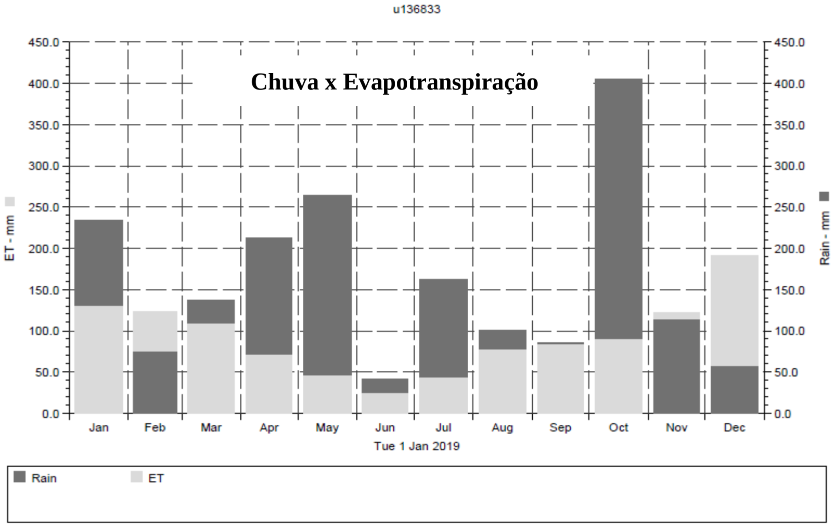
500
1000
1500
2000
2500
Jan
Fev
Mar
Abr
Mai
Jun
Jul
Ago
Set
Out
Nov
Dez
Anual
Precipitação média de 2019
Média precipitação normal de Santa Cruz do Sul entre 1914-1968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Chuva x Evapotranspiração
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Rain - mm
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100.0
150.0
200.0
250.0
300.0
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400.0
450.0
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Apr
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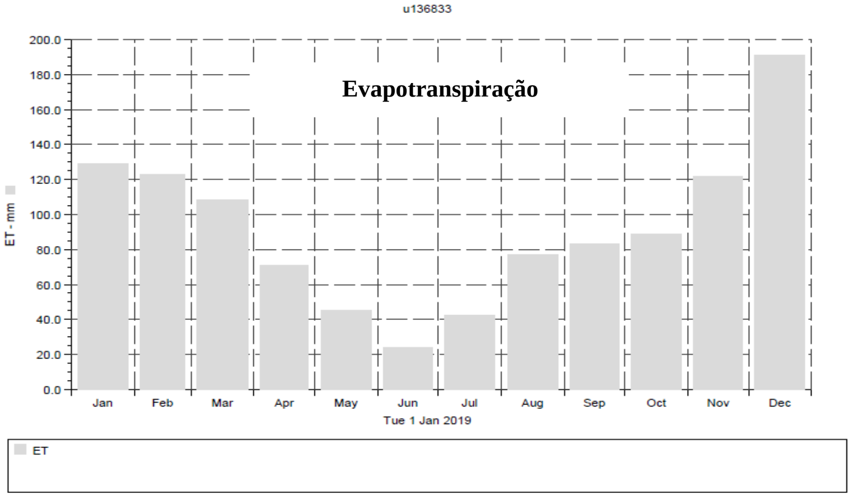
Tue 1 Jan 2019
Rain
ET


u136833
Evapotranspiração
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100.0
120.0
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200.0
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Tue 1 Jan 2019
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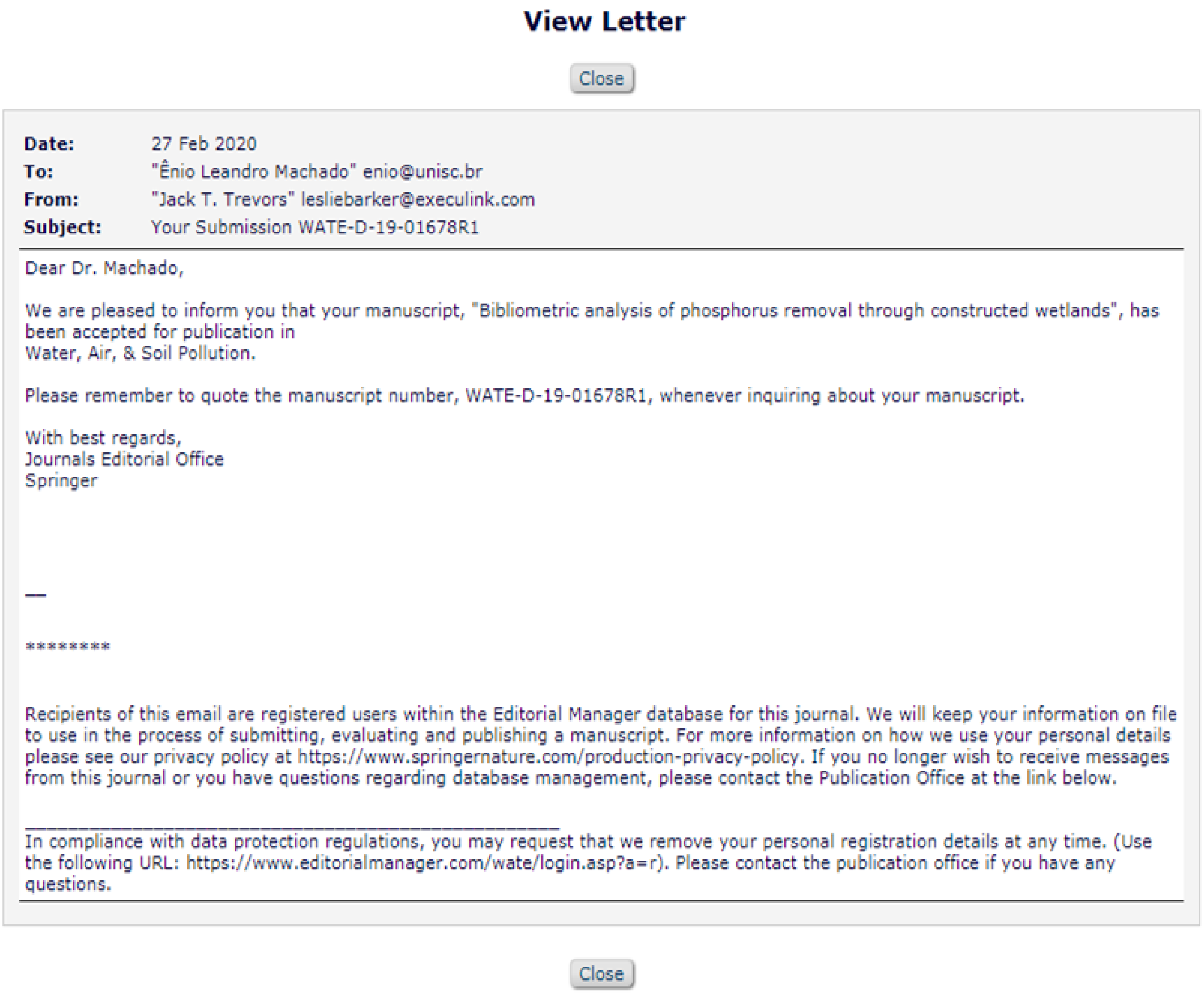
ANEXO III – ACEITE PARA PUBLICAÇÃO DO ARTIGO 1 NA REVISTA *WATER, AIR AND SOIL POLLUTION*.



View Letter

Date: 27 Feb 2020
To: "Ênio Leandro Machado" enio@unisc.br
From: "Jack T. Trevors" lesliebarker@execulink.com
Subject: Your Submission WATE-D-19-01678R1

Dear Dr. Machado,

We are pleased to inform you that your manuscript, "Bibliometric analysis of phosphorus removal through constructed wetlands", has been accepted for publication in
Water, Air, & Soil Pollution.

Please remember to quote the manuscript number, WATE-D-19-01678R1, whenever inquiring about your manuscript.

With best regards,
Journals Editorial Office
Springer

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