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CELY ROLEDO

**AVALIAÇÃO DA CONTAMINAÇÃO NO RIO PARAÍBA DO SUL POR
BISFENOL A (BPA) E DA SUA REMOÇÃO POR ADSORÇÃO**

Bauru
2024

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Tese apresentada como requisito para a obtenção do título de Doutor em Engenharia Civil e Ambiental da Universidade Estadual Paulista "Júlio de Mesquita Filho", Área de Concentração Saneamento Ambiental.

Orientador: Prof. Dr. Adriano Gonçalves dos Reis



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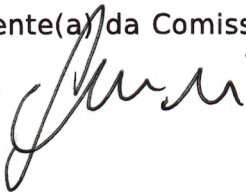
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Aos 01 dias do mês de agosto do ano de 2024, às 08:30 horas, por meio de Videoconferência, realizou-se a defesa de TESE DE DOUTORADO de CELY ROLEDO, intitulada **AVALIAÇÃO DA CONTAMINAÇÃO POR BISFENOL A (BPA) NO RIO PARAÍBA DO SUL E DA SUA REMOÇÃO POR ADSORÇÃO**. A Comissão Examinadora foi constituída pelos seguintes membros: Prof. Dr. ADRIANO GONÇALVES DOS REIS (Orientador(a) - Participação Presencial) do(a) Departamento de Engenharia Ambiental / Unesp - Instituto de Ciência e Tecnologia - Câmpus de São José dos Campos, Prof. Dr. FLÁVIO TEIXEIRA DA SILVA (Participação Virtual) do(a) Departamento de Biotecnologia / Universidade de São Paulo (USP), Prof. Dr. GILSON ALVES QUINÁGLIA (Participação Presencial) do(a) Departamento de Engenharia Ambiental / Faculdades Oswaldo Cruz, Prof.^a Dr.^a MARIA LUCIA PEREIRA ANTUNES SILVA (Participação Virtual) do(a) Departamento de Engenharia Ambiental / Unesp - Instituto de Ciência e Tecnologia - Câmpus de Sorocaba, Prof. Dr. KLEPER DE OLIVEIRA ROCHA (Participação Virtual) do(a) Departamento de Química / Unesp - Faculdade de Ciências - Câmpus de Bauru. Após a exposição pela doutoranda e arguição pelos membros da Comissão Examinadora que participaram do ato, de forma presencial e/ou virtual, a discente recebeu o conceito final: APROVADO. Nada mais havendo, foi lavrada a presente ata, que após lida e aprovada, foi assinada pelo(a) Presidente(a) da Comissão Examinadora.

Prof. Dr. ADRIANO GONÇALVES DOS REIS



PROPOSTA DE ALTERAÇÃO DO TÍTULO

A COMISSÃO EXAMINADORA PROPÕE A ALTERAÇÃO DO TÍTULO DO TRABALHO DA ALUNA: **CELY ROLEDO** DE: "AVALIAÇÃO DA CONTAMINAÇÃO POR BISFENOL A (BPA) NO RIO PARAÍBA DO SUL E DA SUA REMOÇÃO POR ADSORÇÃO"

PARA: AVALIAÇÃO DA CONTAMINAÇÃO NO RIO PARAÍBA DO SUL POR BISFENOL A (BPA) E DA SUA REMOÇÃO POR ADSORÇÃO

Bauru, 01 de agosto de 2024.

A handwritten signature in black ink, appearing to read "Adriano", is written over the printed name of the professor.

Prof. Dr. <ADRIANO GONÇALVES DOS REIS>
Orientador

Dedico essa tese aos meus pais, **Natalia Francisco Roledo** e **Agostinho Roledo** (*in memoriam*), com todo o meu amor, saudades e gratidão.

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Resumo

Este estudo investigou a contaminação por Bisfenol A (BPA) no trecho paulista do rio Paraíba do Sul e propôs um tratamento avançado para sua remoção usando a casca da semente de *Moringa oleifera* como adsorvente. A contaminação por BPA foi quantificada em cinco pontos de captação de água para abastecimento público nos municípios de Santa Branca, Jacareí, São José dos Campos, Tremembé e Aparecida, além de um ponto na cidade de Queluz, ao longo de 2022, com concentrações variando de 11,1 a 116,9 ng L⁻¹, e correlacionada com parâmetros físico-químicos, microbiológicos e bioanalíticos da qualidade da água. A atividade estrogênica foi confirmada em 50% das amostras analisadas, variando de 0,12 a 1,36 ng L⁻¹ de equivalente de estradiol, indicando a presença de múltiplos compostos que contribuem para os efeitos estrogênicos. A avaliação do índice de qualidade da água (IQA) revelou qualidade comprometida nos locais estudados, principalmente no período chuvoso. A correlação entre os parâmetros IQA, concentração de BPA e atividade estrogênica sugere que os compostos desreguladores endócrinos impactam a qualidade da água, condição exacerbada pela infraestrutura inadequada de tratamento de águas residuais. O estudo também investigou a remoção de BPA da água usando casca de semente de *Moringa oleifera* modificada (H-MOH300) como um adsorvente ecológico. As cascas das sementes foram ativadas quimicamente com ácido fosfórico e tratadas termicamente a 300°C. O processo de ativação resultou em um material com área superficial específica de BET de 380 m² g⁻¹ e volume total de poros de 0,282 cm³ g⁻¹. O modelo de isoterma de Langmuir descreveu o processo de adsorção com maior precisão, mostrando capacidade máxima de adsorção de 27,5 mg g⁻¹ a 22°C. A análise termodinâmica revelou que a adsorção foi espontânea e endotérmica, impulsionada principalmente por interações eletrostáticas e π - π . Estudos de regeneração indicaram que a H-MOH300 poderia ser efetivamente reutilizada, sugerindo seu potencial como adsorvente sustentável para remoção de BPA. Este trabalho destaca a necessidade de contínuo monitoramento de contaminantes emergentes em corpos hídricos e a utilidade dos resíduos agrícolas para a remediação ambiental, fornecendo uma solução econômica para a contaminação da água por poluentes emergentes, como o BPA.

Palavras chaves: Contaminantes Emergentes, Bisfenol A, rio Paraíba do Sul, Adsorção, Adsorvente de baixo custo, Carvão ativado, *Moringa oleifera*.

Abstract

This study investigated Bisphenol A (BPA) contamination in the São Paulo stretch of the Paraíba do Sul River and proposed an advanced treatment for its removal using *Moringa oleifera* seed husk as an adsorbent. BPA contamination was quantified at five water catchment sites for public drinking water supply in the municipalities of Santa Branca, Jacareí, São José dos Campos, Tremembé, and Aparecida, as well as one site in the city of Queluz throughout 2022, with concentrations ranging from 11.1 to 116.9 ng L⁻¹, and correlated with physicochemical, microbiological, and bioanalytical water quality parameters. Estrogenic activity was confirmed in 50% of the analyzed samples, ranging from 0.12 to 1.36 ng L⁻¹ estradiol-equivalent, indicating the presence of multiple compounds contributing to estrogenic effects. The water quality index (WQI) evaluation revealed compromised quality at the studied locations, particularly during the rainy season. The correlation between WQI parameters, BPA concentration, and estrogenic activity suggests that endocrine-disrupting compounds impact water quality, exacerbated by inadequate wastewater treatment infrastructure. The study also investigated the removal of BPA from water using modified *Moringa oleifera* seed husk (H-MOH300) as an eco-friendly adsorbent. The seed husks were chemically activated with phosphoric acid and thermally treated at 300°C. The activation process resulted in a material with a BET specific surface area of 380 m² g⁻¹ and a total pore volume of 0.282 cm³ g⁻¹. The Langmuir isotherm model best described the adsorption process, showing a maximum adsorption capacity of 27.5 mg g⁻¹ at 22°C. Thermodynamic analysis revealed that the adsorption was spontaneous and endothermic, primarily driven by electrostatic and π - π interactions. Regeneration studies indicated that H-MOH300 could be effectively reused, suggesting its potential as a sustainable adsorbent for BPA removal. This work highlights the need for continuous monitoring of emerging contaminants in water bodies and the utility of agricultural residues for environmental remediation, providing an economical solution for water contamination by emerging pollutants such as BPA.

Keywords: Emerging Contaminants, Bisphenol A, Paraíba do Sul River, Adsorption, Low-cost adsorbent, Activated carbon, *Moringa oleifera*.

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1 INTRODUÇÃO

Um grande número e quantidade de substâncias são produzidos e consumidos pelo mundo para melhorar a qualidade de vida das pessoas, e resíduos dessas substâncias atingem o meio ambiente contaminando o solo, a água e a atmosfera (MONTAGNER et al., 2019). A crescente urbanização e industrialização contribuem para um aumento significativo da poluição ambiental, especialmente em recursos hídricos.

Algumas dessas substâncias são classificadas como contaminantes emergentes, ou seja, substâncias naturais ou sintéticas que comumente não são monitoradas, mas são encontradas no meio ambiente e podem causar conhecidos ou suspeitos efeitos adversos à saúde humana ou animal (RICHARDSON; KIMURA, 2016). São exemplos de contaminantes emergentes: agrotóxicos, fármacos, hormônios, produtos de higiene pessoal, plastificantes, entre outros (SILVA; COLLINS, 2011).

Entre os poluentes emergentes, o bisfenol A (BPA) tem recebido atenção especial devido às suas propriedades como desregulador endócrino e ampla utilização na produção de plásticos e resinas epóxi. O BPA pode ser encontrado em produtos do cotidiano, como garrafas plásticas, revestimentos internos de latas de alimentos, equipamentos médicos e papéis térmicos, o que facilita sua disseminação no meio ambiente através de resíduos industriais e domésticos (OHORE; ZHANG, 2019).

O impacto do BPA na saúde humana e ambiental é amplamente documentado. Estudos mostram que a exposição ao BPA está associada a efeitos adversos no sistema reprodutivo, desenvolvimento embrionário, sistema nervoso e equilíbrio hormonal (ZHOU et al., 2017; OHORE; ZHANG, 2019).

Devido a esses riscos, a presença de BPA em corpos d'água, especialmente aqueles utilizados para abastecimento de água potável, é uma preocupação significativa. No Brasil, a contaminação por BPA é particularmente preocupante em regiões altamente industrializadas e urbanizadas, especialmente nos estados de São Paulo (MARTINI et al., 2021; MADEIRA et al., 2023), Rio de Janeiro (LOPES et al., 2016; SABINO et al., 2021), e Minas Gerais (CORRÊA et al., 2021; RAMOS et al., 2021).

Montagner et al. (2019) avaliaram a contaminação no estado de São Paulo de 58 contaminantes emergentes entre 2006 e 2015. Compostos como cafeína, 17 β -estradiol, 17 α -etinilestradiol, BPA, atrazina, carbendazina, entre outros, foram considerados de

interesse prioritário dentre os contaminantes estudados devido à frequência de detecção e número de amostras positivas acima do critério de qualidade da água.

A região do Vale do Paraíba paulista, com 39 municípios e situada no eixo das duas maiores metrópoles brasileiras (São Paulo e Rio de Janeiro), é considerada um dos principais eixos de desenvolvimento do estado de São Paulo (OLIVEIRA; QUINTAIROS, 2011). Esta região é parte da bacia hidrográfica do rio Paraíba do Sul, que se estende por territórios pertencentes a três estados da região sudeste: São Paulo, Rio de Janeiro e Minas Gerais (CEIVAP, 2022).

Há diversos fatores que contribuem para a degradação da qualidade das águas da bacia do rio Paraíba do Sul, tais como: a disposição inadequada do lixo; desmatamento indiscriminado; retirada de recursos minerais para a construção civil sem a devida recuperação ambiental; uso indevido e não controlado de agrotóxicos; entre outros. Com relação ao saneamento básico, a situação de degradação é crítica: 1 bilhão de litros de esgotos domésticos, praticamente sem tratamento, são despejados diariamente nos rios da bacia do Paraíba do Sul, pois muitos dos municípios da bacia não contam com estação de tratamento de esgotos (CEIVAP, 2022).

Estudos recentes sobre contaminantes emergentes na bacia hidrográfica do Paraíba do Sul demonstraram contaminação por BPA. Fernandes (2018) em seu estudo sobre o rio Paraíba do Sul na região metropolitana no Rio de Janeiro encontrou concentrações para BPA de 123 a 1581 ng L⁻¹, em 58% das amostras coletadas. Chaves (2016) obteve efetiva detecção de BPA em 16,7% das amostras coletadas no rio Paraíba do Sul na cidade de Aparecida – SP, com concentrações entre 32 e 88 ng L⁻¹. Outro estudo realizado nas cidades de Guararema, São José dos Campos, Taubaté e Pindamonhangaba, apresentou resultados positivos para BPA em 58% das amostras coletadas no rio Paraíba do Sul sendo a maior concentração de 276 ng L⁻¹ (SOUZA et al., 2011). Tais estudos demonstram que o BPA é um contaminante emergente de interesse também na bacia hidrográfica do rio Paraíba do Sul. Porém, não há estudos correlacionando esta contaminação com outros parâmetros de qualidade da água.

O processo convencional de tratamento de água de abastecimento, conhecido por ciclo completo, é composto pelas etapas de coagulação, floculação, sedimentação e filtração, o qual apresenta baixas taxas de remoção do BPA. No Brasil, estudos demonstram taxas de remoção de BPA na faixa de 30% para o tratamento de ciclo completo (LIMA et al., 2017; FERNANDES, 2018), e considerando que cerca de 75% do

volume de água tratada no país é pelo ciclo completo (IBGE, 2017), é provável de se encontrar este contaminante na água potável onde a fonte estiver contaminada.

Para enfrentar o desafio da contaminação por BPA na água, diversas abordagens têm sido investigadas, incluindo processos de degradação enzimática, oxidação avançada, oxidação com permanganato, tratamento fotocatalítico e osmose reversa (OHORE; ZHANG, 2019). No entanto, essas tecnologias muitas vezes enfrentam limitações significativas, como altos custos operacionais, consumo elevado de energia e geração de subprodutos tóxicos (TURSI et al., 2018; MPATANI et al., 2021).

Em contraste, a adsorção tem se destacado como uma técnica promissora devido à sua eficiência (BAUTISTA-TOLEDO et al., 2014). Entretanto, a aplicação em larga escala de carvão ativado comercial também é limitada pelo seu alto custo e pela alta necessidade energética para regeneração (MPATANI et al., 2021). Pesquisas recentes em adsorção têm se concentrado na busca de métodos alternativos para reduzir o custo de produção dos carvões ativados comercialmente disponíveis (RECK et al., 2018) já que o custo operacional do tratamento de água pode aumentar em até 100% adicionando um sistema de adsorção por carvão ativado ao ciclo completo (MIERZWA et al., 2008).

Nesse contexto, a utilização de resíduos agrícolas como adsorventes de baixo custo e ecologicamente favoráveis surge como uma alternativa promissora. Estudos sobre o processo de adsorção para a remoção de BPA têm apresentado resultados encorajadores, como por exemplo, a adsorção com carvão ativado da *Musa acuminata*, com capacidade máxima de adsorção ($q_{\text{máx}}$) de 1,30 mg g⁻¹ (RAHMAT et al., 2019); a adsorção com carvão ativado da biomassa da *Tithonia diversifolia*, com $q_{\text{máx}}$ de 15,69 mg g⁻¹ (SUPONG et al., 2019); e adsorção com a superfície modificada da celulose da Vassoura espanhola, com $q_{\text{máx}}$ de 4,86 mg g⁻¹ (TURSI et al., 2018). Portanto, o processo de adsorção com adsorventes naturais de baixo custo se apresenta como uma proposta viável de tratamento de água para a remoção do BPA.

A *Moringa oleifera*, uma planta amplamente cultivada em regiões tropicais (MPATANI et al., 2020), é conhecida por suas múltiplas aplicações, incluindo o uso de suas sementes como coagulante natural em tratamentos de água e esgoto (RIBEIRO et al., 2019; CHALES et al., 2022; BATISTA et al., 2023). Contudo, a utilização das cascas das sementes de *Moringa oleifera* como adsorventes ainda é pouco explorada. Essas cascas, frequentemente descartadas como resíduos, possuem potencial para serem transformadas em materiais adsorventes eficientes após modificações químicas e térmicas com o objetivo

de aumentar sua área superficial, propriedade essencial para uma efetiva adsorção (YANG et al., 2020).

Portanto, devido à importância da atuação como desregulador endócrino do BPA e sua identificação na bacia hidrográfica do rio Paraíba do Sul, uma região altamente povoada, urbana e industrializada, este estudo fez um mapeamento da contaminação de BPA e atividade estrogênica nos pontos de captação de água para abastecimento público ao longo do trecho paulista do rio Paraíba do Sul correlacionando com outros parâmetros de qualidade da água e avaliou sua remoção via tratamento avançado utilizando biomassa da casca da semente da *M. oleifera* modificada como adsorvente ecológico, tornando um estudo ímpar na literatura.

Essa tese é apresentada na forma de dois artigos científicos. O primeiro avalia a concentração de BPA e a atividade estrogênica em diferentes pontos do rio Paraíba do Sul – trecho paulista, correlacionando esses dados com o índice de qualidade da água e a infraestrutura de tratamento de efluentes na região. O segundo artigo explora o potencial da casca de semente de *Moringa oleifera* modificada como um adsorvente de baixo custo para a remoção de BPA, avaliando a eficiência do processo de adsorção, características termodinâmicas e cinéticas, e a viabilidade de reutilização do adsorvente.

Ao abordar esses dois aspectos, esta tese contribui para a compreensão dos desafios e das soluções na gestão de contaminantes emergentes, em especial o bisfenol A, promovendo abordagens sustentáveis e inovadoras para o seu monitoramento e sua remoção de águas contaminadas. Esta tese se enquadra aos Objetivos de Desenvolvimento Sustentável da ONU nº 6 (Assegurar a disponibilidade e gestão sustentável da água e saneamento para todos) e nº 12 (Consumo e produção responsáveis), e nas áreas de tecnologia prioritárias definidas pelo MCTIC de Tecnologias para o Desenvolvimento Sustentável (setor V – Tratamento de Poluição) e de Tecnologias para Qualidade de Vida (setor II – Saneamento Básico).

2 OBJETIVOS

2.1 Objetivo Geral

Este estudo busca avaliar a contaminação por BPA no trecho paulista do rio Paraíba do Sul e propor a sua remoção via tratamento avançado com o uso da casca da semente da *Moringa oleifera* como adsorvente.

2.2 Objetivos Específicos

- Quantificar a contaminação por BPA e atividade estrogênica em pontos de captação de água para abastecimento público no trecho paulista do rio Paraíba do Sul e correlacionar com a qualidade da água do rio (parâmetros físico-químicos, microbiológicos e bioanalíticos).
- Propor e avaliar tratamento avançado para a remoção do BPA por adsorção com a casca da semente de *Moringa oleifera*, assim como diferentes métodos de ativação e regeneração do adsorvente.

3 ARTIGO SOBRE A CONTAMINAÇÃO DE BPA DO RIO PARAÍBA DO SUL

3.1 A Comprehensive Study on Bisphenol A and Estrogenic Activity in the Paraíba do Sul River, São Paulo, Brazil

ABSTRACT

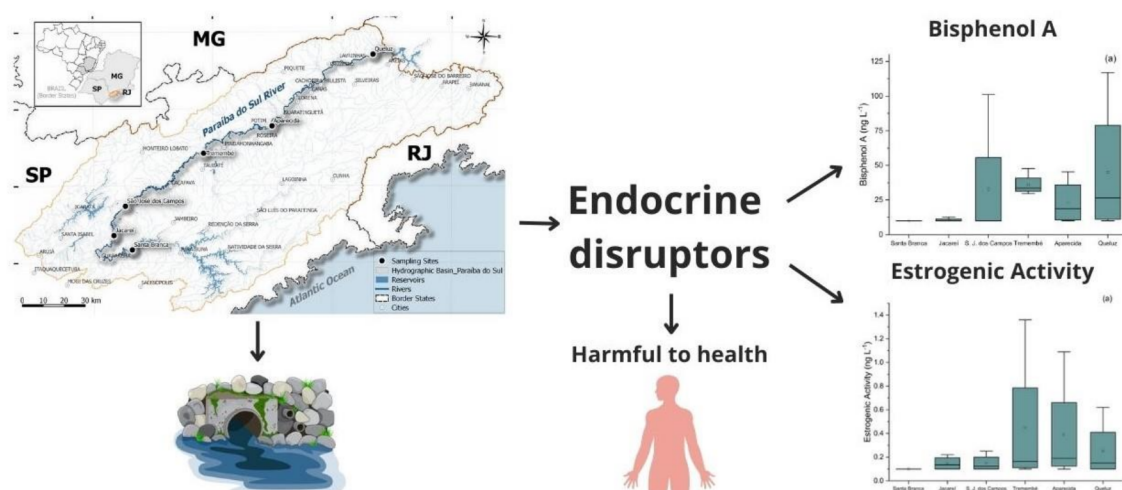
In recent decades, contaminants of emerging concern (CECs) in aquatic environments have garnered significant attention due to their adverse effects on ecosystems and human health. Among these CECs, bisphenol A (BPA) is a major concern because of its widespread use and endocrine-disrupting properties. Brazil's urbanization and industrial growth have led to significant pollution challenges, primarily due to inadequate sewage infrastructure and untreated domestic wastewater being discharged into rivers, contributing to the presence of emerging contaminants in surface waters. This study assessed BPA contamination and estrogenic activity in the Paraíba do Sul River in São Paulo State, Brazil. BPA was quantified in 50% of the samples, with concentrations ranging from 11.1 to 116.9 ng L⁻¹. The estrogenic activity assay also showed positive results in 50% of the samples, ranging from 0.12 to 1.36 ng L⁻¹ of estradiol-equivalent, indicating the presence of multiple compounds contributing to estrogenic effects. This underscores the need for a comprehensive approach to monitoring water quality. The water quality index (WQI) revealed compromised water quality at the studied sites, particularly during the rainy season. The correlation between the WQI, BPA, and estrogenic activity parameters suggests that endocrine-disrupting compounds impact water quality, exacerbated by inadequate wastewater treatment infrastructure.

Keywords: BLYES, BPA, contaminants of emerging concern, endocrine disruptor, water quality index

HIGHLIGHTS

- *Positive results were found for BPA and for estrogenic activities in 50% of the samples.*
- *Other endocrine disruptors contribute to the levels of estrogenic activity.*
- *Poor wastewater treatment infrastructure contributes to river contamination.*

GRAPHICAL ABSTRACT



Introduction

The introduction of various substances into the environment, originally intended to enhance diverse aspects of quality of life, has inadvertently contaminated natural resources, including soil, water, and the atmosphere (Montagner et al. 2019). Despite the reduction in the emission of some pollutants, such as pesticides, polychlorinated compounds, aromatic hydrocarbons, and heavy metals, in surface waters, because of the approval of laws that regulate issues related to pollution, the presence of contaminants of emerging concern (CECs) has become a new challenge (Al-Odaini et al. 2013).

Pollutants that are classified as CECs are natural or artificial substances found in the environment that may cause adverse effects on humans or animals but are not commonly monitored (Madeira et al. 2023). Examples of CECs include pesticides, drugs, hormones, personal care products, and plasticizers (Montagner et al. 2019; Madeira et al. 2023). Generally, conventional domestic effluent treatment systems, consisting of preliminary, primary, and secondary treatments, cannot satisfactorily remove these contaminants (Ribeiro et al. 2015), as these contaminants are found in reduced concentrations of ng L^{-1} or $\mu\text{g L}^{-1}$.

Among the CECs are endocrine disruptors, which are compounds that can interfere with the production or action of hormones, and they can cause damage to the reproductive and immune systems of higher organisms, especially aquatic organisms. These substances can either block or mimic the activity of natural hormones, which can interfere with the reproductive systems of both humans and animals (Joseph et al. 2013).

Due to the large number of synthetic chemicals currently produced and the fact that the endocrine-disrupting potential of a compound cannot be readily determined by the functional groups present in its molecular structure, the identification and monitoring of endocrine disruptors are highly important (Wang 2016). Moreover, these substances can reach the environment from various anthropogenic sources and reach different environmental matrices (Martini et al. 2021).

The substance 2,2-bis(4-hydroxyphenyl) propane, known as bisphenol A (BPA), is obtained by combining two phenol molecules with one acetone at acidic pH and high temperatures. BPA is used to produce epoxy resins and polycarbonate plastics, phenol resins, polyacrylates and polyesters, and food packaging. It is considered a CEC of interest because it acts as an endocrine disruptor (Ohore i Songhe 2019).

Bisphenols, which mimic several hormones, such as estrogen, can also have health implications in humans, including sex-specific low neurodevelopment, uterine cancer, immune toxicity, neurotoxicity, and interference with cellular pathways (Ohore i Songhe 2019). *In vivo* experiments demonstrated that exposure to a dose of 100 $\mu\text{g kg}^{-1}$ of BPA caused high insulin levels, slight insulin resistance, and glucose intolerance in adult male mice, similar to the effects of 17- β -estradiol (E2) (Alonso-Magdalena et al. 2012).

BPA is also important because an estimated 10 million tons are produced annually, making it one of the most significant chemicals produced worldwide (U.S. EPA 2023). BPA is used in the industrial production of plastic bottles, can linings, thermal papers, etc. Its presence in the environment has raised questions about its potential impacts, especially on children's health (Zhou et al. 2017).

The water pollution problem seems to be more acute in developing countries, such as Brazil, since untreated wastewater is frequently released into the environment, and this is the primary source of estrogenic compounds in surface waters (Tue et al. 2023). The Brazilian population (ca. 203 million inhabitants) is concentrated in urban areas (IBGE 2022). The resulting intense land use, insufficient sewage disposal, and inadequate treatment infrastructure negatively affect water quality (Dias et al. 2015).

The number of studies evaluating the occurrence of CECs in Brazil is limited. Nevertheless, some reviews on CECs in Brazil demonstrate the prominent presence of caffeine, drugs, hormones, and bisphenol A in surface waters (Montagner et al. 2019; Starling et al. 2019; Madeira et al. 2023).

Only 29.2% of all generated domestic sewage is treated in Brazil (SNIS 2022). Most of the rest is released untreated into rivers, which are the population's primary water

sources. Regarding the monitoring of CECs in Brazilian wastewater treatment facilities, studies have shown that conventional (up to the secondary treatment stage) treatment plants, even when they do exist, are inadequate for removing these compounds (Starling et al. 2019). Regarding BPA contamination in freshwaters used as a source of drinking water after treatment in Brazil, studies show its occurrence, especially in the most industrialized and urbanized states. In São Paulo, BPA concentrations have been reported by Martini et al. (2021) and Madeira et al. (2023), ranging from 6.5 to 1300 ng L⁻¹ and 13.1 to 895 ng L⁻¹, respectively. In Rio de Janeiro, studies by Lopes et al. (2016) and Sabino et al. (2021) documented BPA levels ranging from 1.37 to 39.86 µg L⁻¹ and 0.03 to 1.16 µg L⁻¹, respectively. In Minas Gerais, Corrêa et al. (2021) and Ramos et al. (2021) reported concentrations ranging from 5.8 to 1587.8 ng L⁻¹ and 0.45 to 3.01 µg L⁻¹, respectively.

Although endocrine disruptors have harmful effects on organisms' health, Brazil has no specific regulation for their presence in water for human consumption (Starling et al. 2019). The difficulty of removing chemical substances such as emerging contaminants, including BPA, from sewage and water treatment plants represents a significant barrier to controlling their dissemination in the aquatic environment.

The conventional drinking water treatment process involves coagulation, flocculation, sedimentation, filtration, and disinfection stages and has low BPA removal rates. In Brazil, studies have demonstrated BPA removal rates in the range of 30% for conventional treatment (Lima et al. 2017). Although Teixeira et al. (2021) verified lower concentrations of BPA in treated water after disinfection than those in raw water, chlorination could generate chlorinated derivatives of Bisphenol A that could also cause health problems (Plattard et al. 2021). Considering that approximately 75% of the water that is treated in Brazil is treated by conventional treatment (IBGE 2017), BPA is likely to be found in drinking water for which the source is contaminated with BPA.

The Paraíba do Sul River, formed by the confluence of the Paraitinga and Paraíba Rivers in the state of São Paulo, extends over 1,150 kilometers, providing a critical water resource to 184 municipalities across São Paulo, Minas Gerais, and Rio de Janeiro. The basin sustains over 5.2 million residents (IBGE 2022) and is a key economic hub, contributing approximately 13% of Brazil's gross domestic product (GDP) and supplying 85% of the water to the Rio de Janeiro metropolitan area, which supports over 12 million inhabitants (OECD 2017). There is also a recent water transfer from the Jaguari River (a Paraíba do Sul tributary) to the dams of the Cantareira System, which is

responsible for the water supply for almost 9 million people in the São Paulo metropolitan area (ANA [sense data]).

Despite its economic and social significance, the Paraíba do Sul River basin is beset by severe environmental challenges. Water quality has significantly deteriorated, largely due to inadequate waste management practices, widespread deforestation, unregulated extraction of mineral resources, and the excessive application of pesticides. Compounding these issues, approximately one billion liters of untreated domestic sewage are discharged daily into the river, underscoring the urgent need for enhanced sanitation infrastructure (CEIVAP [sense data]). Given the basin's crucial role in supplying drinking water to Brazil's largest metropolitan regions and the ongoing conflicts over water use (ANA 2016), there is a pressing need for further studies to evaluate and improve water quality within this essential watershed.

Research on CECs in the Paraíba do Sul River Basin is sparse, with limited studies indicating bisphenol A (BPA) contamination, particularly in the São Paulo section. Notably, a study found BPA in 58% of water samples from key cities along the river (Souza et al. 2011). However, there is a critical need for comprehensive research to assess the extent of BPA contamination, its seasonal dynamics, and correlations with other water quality parameters. Such research is vital for informing policies and protecting both public health and the sustainability of this essential water resource.

Hence, this study aimed to investigate bisphenol A (BPA) contamination, specifically within the São Paulo State stretch of the Paraíba do Sul River. The primary objective is to comprehensively assess the extent of BPA pollution in this region. Additionally, we aim to analyse the level of estrogenic activity to gain insights into potential endocrine-disrupting effects. Through this investigation, we seek to elucidate seasonal variations in BPA concentrations and identify possible sources of contamination contributing to its presence in the river.

Materials and Methods

CETESB, the São Paulo State Environmental Agency, has operated the Surface Water-Quality Monitoring Program since the 1970s. This program involves testing the chemical, microbiological, hydrobiological, and toxicological aspects of surface water samples collected from various locations across the state of São Paulo, Brazil. (Roubicek et al. 2020). Currently, it comprises more than 500 sampling sites from different state river basins. The analysed and interpreted data are available in Portuguese to the general public

in annual reports on their website. CETESB uses all the results to prioritize pollution control actions, identify degraded sites, and verify the conditions for aquatic life protection and other water uses, such as irrigation, livestock, and recreation. As part of the water quality evaluation, CETESB calculates, among other indices, the water quality index (WQI) for each site.

The WQI is calculated by the weighted multiplication of water qualities corresponding to the variables that make up the Index (CETESB 2023), according to equation 1:

$$WQI = \prod_{i=1}^n q_i^{w_i} \quad (1)$$

where WQI is a number between 0 and 100; q_i is the quality of the i^{th} parameter, a number between 0 and 100, obtained from the respective “average quality variation curve”, depending on its concentration or measure; w_i is the weight corresponding to the i^{th} parameter, a number between 0 and 1, assigned depending on its importance for the overall quality conformation; and n is the number of variables included in the WQI calculation.

The quality variables, which are part of the WQI calculation, mainly reflect the contamination of water bodies by the release of domestic sewage. It comprises the following parameters, including w_i , the limit of detection (LOD), and the limit of quantification (LOQ): *Escherichia coli* ($w_i=0.15$, LOD = 1 CFU (100 mL)⁻¹), biochemical oxygen demand (BOD) ($w_i=0.10$, LOD = 1 mg L⁻¹, LOQ = 2 mg L⁻¹), total nitrogen ($w_i=0.10$, LOD = 0.1 mg L⁻¹, LOQ = 0.5 mg L⁻¹), total phosphorus ($w_i=0.10$, LOD = 0.003 mg L⁻¹, LOQ = 0.02 mg L⁻¹), temperature ($w_i=0.10$, LOD = 0.1 °C, LOQ = 1 °C), pH ($w_i=0.12$, LOD = 0.03, LOQ = 0.1), turbidity ($w_i=0.08$, LOD = 1.0 NTU, LOQ = 5 NTU), total solids ($w_i=0.08$, LOD = 10 mg L⁻¹, LOQ = 50 mg L⁻¹), and dissolved oxygen ($w_i=0.17$, LOD = 0.1 mg L⁻¹, LOQ = 0.5 mg L⁻¹) (CETESB 2023). The analytical methods and curves for the WQI are described in the supplementary material. As the WQI variables were collected simultaneously as the sample collections for BPA quantification and estrogenic activity assay, this study used the WQI calculated for correlation purposes for the sites studied.

Study Area and Sample Collection

The São Paulo stretch of the Paraíba do Sul River comprises its formation at the confluence of the Paraitinga and Paraibuna Rivers to the Rio de Janeiro State border. With more than 2 million inhabitants in 39 municipalities (IBGE 2022), this is the first stretch of the Paraíba do Sul River before it enters the states of Rio de Janeiro and Minas Gerais.

The water samples were collected from six sampling sites that belonged to CETESB's Surface Water-Quality Monitoring Program (Figure 1) (CETESB 2022); five of them are used as source waters to produce drinking water for the municipalities of Santa Branca, Jacareí, São José dos Campos, Tremembé, and Aparecida. The sixth site, at the municipality of Queluz, is the closest site on the Rio de Janeiro state border. Samples were obtained from each site in February, May, August, and October 2022. Information about the municipalities and the sample site coordinates is shown in Table 1.

Table 1 Municipal data and sample site coordinates

Municipality	Population ¹	Urbanized área ¹ (km ²)	Sewage Service ²		Organic Matter Load ² (kg BOD day ⁻¹)		Sample Site coordinates
			Collection (%)	Treatment (%)*	Potential	Remaining	
Santa Branca	13,975	5.78	64.0	5.0	711	697	23° 22' 32'' S 45° 53' 12'' W
Jacareí	240,275	50.33	98.2	99.1	12,628	3,108	23° 18' 48'' S 45° 58' 20'' W
São José dos Campos	697,054	128.94	94.4	99.2	39,005	7,243	23° 11' 16'' S 45° 55' 04'' W
Tremembé	51,173	10.85	98.6	100	2347	79	22° 57' 40'' S 45° 33' 10'' W
Aparecida	32,569	6.26	70.0	0.0	1,927	1,927	22° 50' 40'' S 45° 14' 04'' W
Queluz	9,159	2.42	77.2	85.0	611	238	22° 32' 32'' S 44° 46' 26'' W

¹ (IBGE 2022) ² (CETESB 2023) *Treatment % means quantity of collected sewage that is treated

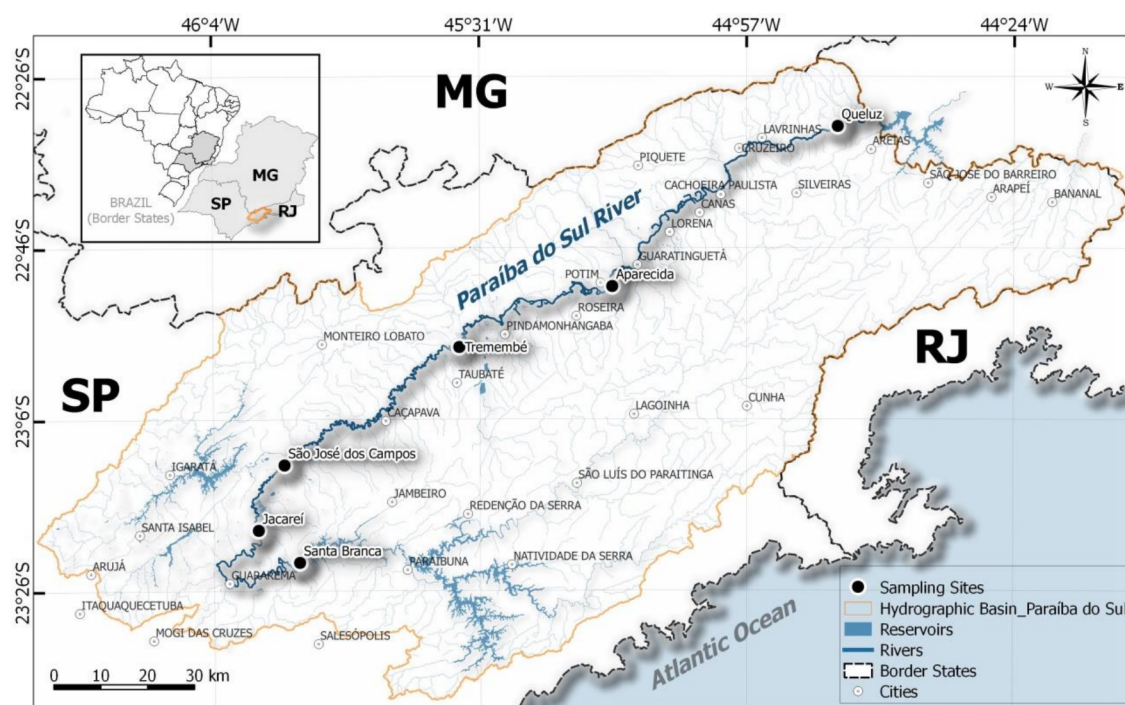


Figure 1 Sampling sites at the Paraíba do Sul River in the state of São Paulo, Brazil

Water samples were collected using 1 L amber flasks for each analysis, BPA quantification and estrogenic activity assay, and preserved according to Standard Methods for the Examination of Water and Wastewater (APHA 2023). For comparison purposes, the sampling campaigns for the estrogenic activity assay and BPA analysis were run simultaneously with the sampling of the CETESB's Surface Water-Quality Monitoring Program. Each sample collection obtained all the complementary parameters for WQI calculations.

Solid-phase extraction

Samples for BPA analysis and estrogenic activity assays were previously concentrated using solid phase extraction.

Samples were extracted using an automated system (SPE DEX 4790, Horizon Technology, Salem, NH) coupled with Oasis HLB cartridges, obtained from Waters (Milford, MA, USA), according to USEPA method 1694 (U.S. EPA 2008). The cartridges were conditioned with 15 mL of methanol and 10 mL of water. One litre of water sample was extracted. The cartridge was dried for 20 minutes using nitrogen, and the analytes were eluted with 15 mL of methanol. The eluate was evaporated using a Genevac EZ-2 evaporator, and the sample was reconstituted in 1 mL of 10% Dimethyl sulfoxide (in water) for the BLYES assay.

For BPA analysis, the sample was reconstituted in 1 mL of methanol for subsequent analysis by liquid chromatography coupled to sequential mass spectrometry.

Liquid Chromatography–Mass Spectrometry

The 1200 chromatographic system from Agilent (Santa Clara, CA, USA) connected to a 6410 triple quadrupole mass spectrometer from Agilent (Santa Clara, CA, USA) was used for liquid chromatography-tandem mass spectrometry analysis. Precisely 10 μL of the sample was injected into a ZORBAX SB-C18 column (30 mm $\times$ 2.1 mm, 3.5 μm particle size) from Agilent (Santa Clara, CA, USA) at 30 $^{\circ}\text{C}$. The mobile phase used for the analysis consisted of 0.01% (v/v) ammonium hydroxide in water and methanol, which was previously filtered through a 0.2 μm porous membrane at a flow rate of 0.3 mL min^{-1} . The following gradient was used: 0 min 30%, 3 min 70%, 6 min 90%, 12 min 90%, and 13 min 30% methanol. The chromatographic column effluent was directed to the mass spectrometer through the electrospray ionization source, and it was monitored by selected reaction monitoring (SRM). The ionization source was operated in negative ion mode. The instrumental limits of detection and quantification were obtained by the signal-to-noise ratio (SNR) method, which compares the analytical signal of the standards with the baseline noise. The LOD was determined with an SNR of 3:1, and the LOQ was determined with an SNR of 10:1, with values of 5 and 10 $\mu\text{g L}^{-1}$, respectively. Santos et al. (2022) and Madeira et al. (2023) describe the quality data and recovery tests.

Estrogenic Activity Assay

Estrogenic activity was determined using *Saccharomyces cerevisiae* BLYES strains (Bioluminescent Yeast Estrogen Screen). Yeast cells were cultured, and the assay was carried out as described by Sanseverino et al. (2005). *Saccharomyces cerevisiae* cells do not naturally have receptors for estrogens or androgens. This BLYES yeast strain is genetically modified to respond to estrogenic agents by the insertion of the gene to express the human estrogen receptor (hER- α). In this system, the hER- α produced binds to estrogen response elements, which have been inserted into a strong promoter on a plasmid. This promoter controls the expression of the *luxA* and *luxB* genes, which were originally obtained from luminescent bacteria, were also inserted into the plasmid and are responsible for luminescence production. Yeast can emit light when in contact with a substance that binds to hER, activating the promoter (Sanseverino et al. 2005).

The sample extracts and a 17- β -estradiol (E2) standard solution were serially diluted in dimethylsulfoxide, and 100 μ L was transferred to a 96-well microtiter plate. Next, 100 μ L of seeded yeast medium was added to the wells. The plates were then sealed and shaken on a vortex for approximately 20 seconds. After incubation for four hours at 30 $^{\circ}$ C, the luminescence was read using a plate reader (Victor X3). In each test, water, dimethylsulfoxide and E2 (serially diluted) were used as blank solvents and positive controls.

The results were expressed quantitatively through the equivalent estrogenic activity (ng L⁻¹ of estradiol-equivalent or EEQ) using effect curves produced with the tested concentrations of 17- β -estradiol (CETESB 2020). The LOD and LOQ are 0.03 and 0.1 ng L⁻¹ of estradiol-equivalent or EEQ, respectively.

Results and Discussion

Estrogenic Activity

Estrogenic activity was quantified in 50% of the samples, ranging from 0.12 to 1.36 ng L⁻¹ of estradiol-equivalent (Figure 2). It was not detected at the Santa Branca site. Higher results were observed in October, with the Tremembé and Aparecida sites presenting results of more than 1 ng L⁻¹ of estradiol-equivalent, which is sufficient to cause significant adverse estrogenic effects (Dias et al. 2015; CETESB 2018).

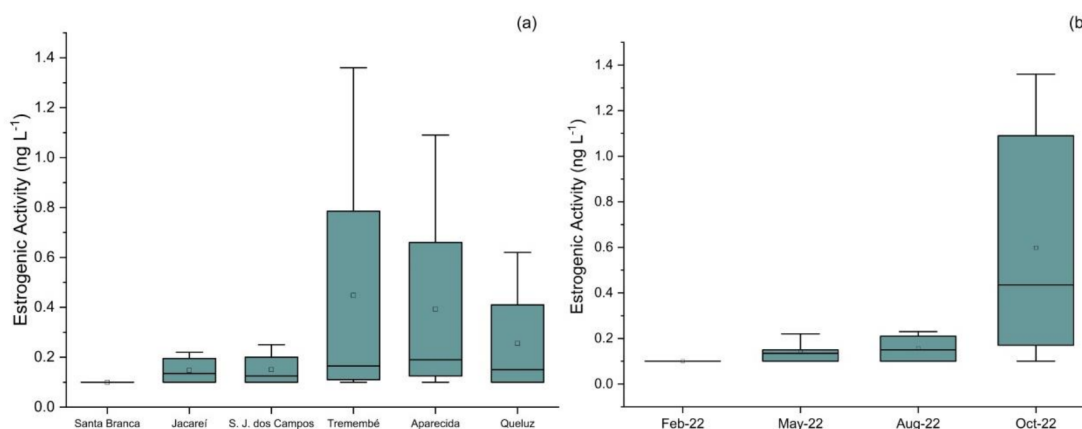


Figure 2 Box plots for estrogen activity (of estradiol-equivalent) at different river sites (a) and during different periods (b). The box ranges between the 25th and 75th percentiles, the whiskers show the lowest and highest values, respectively, and the horizontal bar is the median concentration (n=24, positive n=12). If the result found is less than the LOQ, the LOQ value is considered.

Among the 27 sites from the monitoring program in the state of São Paulo where estrogenic activity was evaluated in 2022, 14 showed average annual estrogenic activity higher than 1.0 ng L⁻¹ of estradiol-equivalent, which is considered high activity (CETESB

2023). Previous studies (CETESB 2018) have shown that estrogenic activity can be correlated with total nitrogen, indicating that the assay detects compounds from domestic sewage origin, such as natural or synthetic hormones. Figure 3 (a) shows the total nitrogen concentrations, and by comparing the results of estrogenic activity from Figure 2 (a), it can be inferred that the higher estrogenic activity found at Tremembé correlates with the higher nitrogen concentration at the same spot. The linear correlation (R^2) between the estrogenic activity mean values for 2022 and the total nitrogen concentrations at each site were 0.6472 is presented at Figure 3 (b). There was no correlation between estrogenic activity and other parameters evaluated.

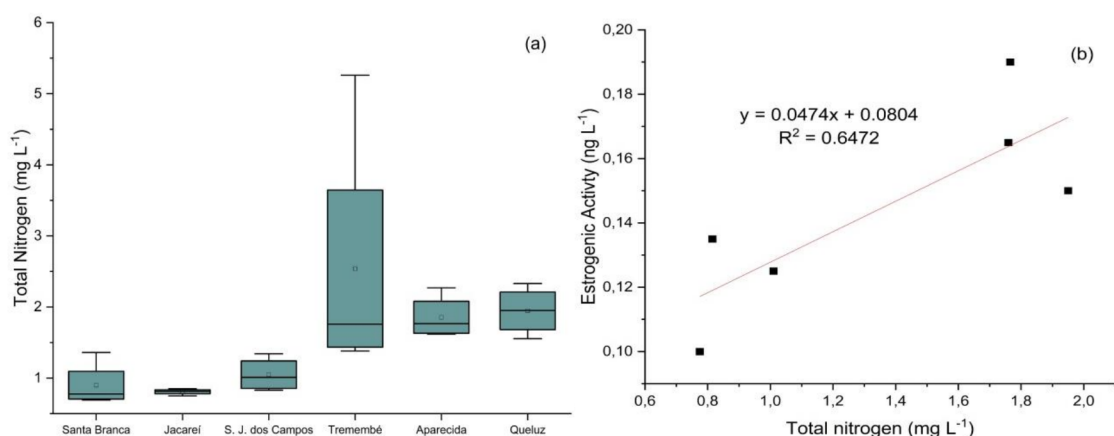


Figure 3 Box plots for total nitrogen concentrations for 2022 period (a) (CETESB 2023). The box ranges between the 25th and 75th percentiles, the whiskers show the lowest and highest values, respectively, and the horizontal bar is the median concentration (n=24, positive n=12) and linear correlation between estrogenic activity and total nitrogen mean concentrations (b). If the result found is less than the LOQ, the LOQ value is considered.

Dias et al. (2015) evaluated the estrogenic activity at the Paraíba do Sul River in the Rio de Janeiro State stretch. According to these authors, the levels of estrogenic activity in the water samples from the Paraíba do Sul River appear to rise as the river passes through the municipalities. This behavior is also observed in our evaluation, in which the three last municipalities present higher results than the three first cities. An increase in estrogenic activity is observed after the most populated cities, decreasing after the town of Tremembé, where the least populated cities are located (Table 1).

BPA Quantification

BPA was quantified in 50% of the samples, ranging from 11.1 to 116.9 ng L⁻¹ (Figure 4). The lowest levels of BPA were detected at the sampling site of Santa Branca (lower than the quantification limit of 10 ng L⁻¹) [Figure 4 (a)], which is a clean area that is

less urbanized and has practically no industry. Similar results were reported by Czarzyńska-Goślińska et al. (2017).

The highest concentration of BPA (116.9 ng L^{-1}) was detected at Queluz. Despite being a small city with no relevant industrial activity, it is located downstream of industrialized municipalities with lower levels of wastewater treatment in the region, such as Guaratinguetá and Cruzeiro, which present remaining loads of organic matter of 4.9 and 4.2 tons of $\text{BOD}_{5,20}$ per day, respectively (CETESB 2023).

The Tremembé site showed positive results in 100% of the samples, ranging from 29.5 to 47.7 ng L^{-1} , probably due to its location downstream of São José dos Campos, which is the region's most populated, urbanized, and industrialized municipality. Although the municipality treats almost 94,4% of its urban sewage, the remaining loads of organic matter are 7.2 tons of $\text{BOD}_{5,20}$ per day (Table 1).

In 2022, the remaining loads of organic matter in sewage in the São Paulo stretch of the Paraíba do Sul River were estimated to be 37 tons of $\text{BOD}_{5,20}$ per day (CETESB 2023).

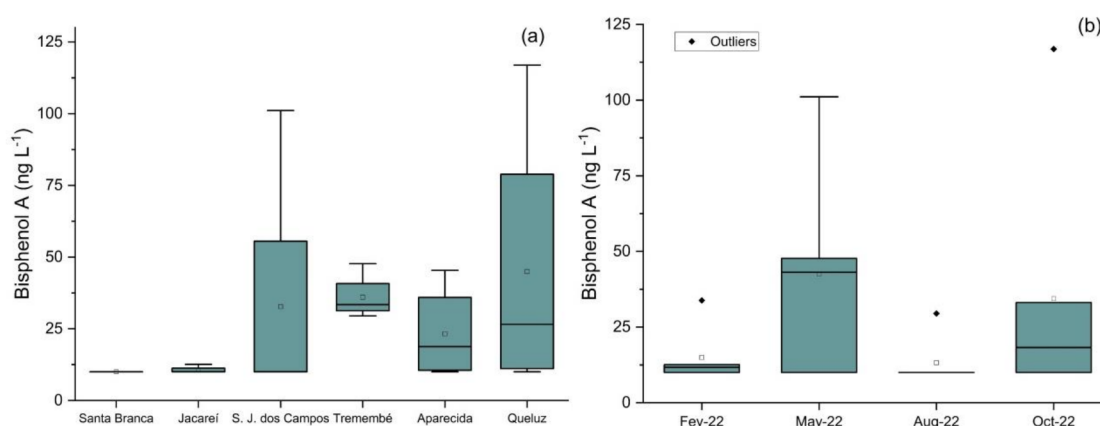


Figure 4 Box plots for bisphenol A determined at different river sampling points (a) and during different periods (b). The box ranges between the 25th and 75th percentiles, the whiskers show the lowest and highest values, respectively, and the horizontal bar is the median concentration ($n=24$, positive $n=12$). If the result found is less than the LOQ, the LOQ value is considered.

The results presented in Figure 4 (b) show that there is no evident seasonal influence on BPA concentrations because May (autumn) and August (winter) are dry seasons (less than 100 mm of rain monthly), and February (summer) and October (spring) are rainy seasons (more than 100 mm of rain monthly). The highest concentrations of BPA occurred in the May and October campaigns. Czarzyńska-Goślińska et al. (2017) also did not find a correlation between BPA concentrations and seasonal influence in their study in

Poland, with concentrations between 5 and 95 ng L⁻¹, similar to the Paraíba do Sul River, which has concentrations ranging between 11.1 and 116.9 ng L⁻¹.

Montagner et al. (2019) evaluated the presence of 58 emerging contaminants in the state of São Paulo between 2006 and 2015. BPA was quantified in almost 67% of samples analysed in a wide range of concentrations, between 2 and 13,016 ng L⁻¹. According to the authors, the highest BPA levels were observed at sampling sites influenced by industrial and densely populated areas. In their study, Martini et al. (2021) also concluded that regions with more industrial activity have considerably higher BPA concentrations.

Table 2 compares the highest levels of BPA contamination quantified in the Paraíba do Sul River with those in other regions of Brazil and with those of international papers that evaluated BPA contamination in surface waters between 2015 and 2021. The analyses show that the BPA levels reported in this study are similar to those in most other monitored Brazilian rivers. The Paraíba do Sul River also shows BPA contamination levels similar to those of the South Platte River in the United States (Bai et al. 2018) and the Hogsmill River in the United Kingdom (Wilkinson et al. 2017).

Table 2 Comparison of the maximum BPA concentrations in Brazil's surface waters between 2015 and 2021

Waterbody	Region	Maximum	
		(ng L ⁻¹)	References
Bolonha Reservoir	Pará, Brazil	115	(Teixeira et al. 2021)
João Mendes River	Rio de Janeiro, Brazil	1,160	(Sabino et al. 2021)
Guarapiranga Reservoir	São Paulo, Brazil	270	(Martini et al. 2021)
Cascata Reservoir	São Paulo, Brazil	370	
Jaguari Reservoir	São Paulo, Brazil	460	
Ribeirão Grande	São Paulo, Brazil	150	
Ribeirão Pires	São Paulo, Brazil	200	
Araras River	São Paulo, Brazil	420	
Jaguari River	São Paulo, Brazil	1,300	
Piracicaba River	São Paulo, Brazil	124	
São Miguel Arcanjo River	São Paulo, Brazil	144	
Sapucaí Guaçu River	São Paulo, Brazil	138	
Paraopeba River Basin	Minas Gerais, Brazil	1,587	(Corrêa et al. 2021)
Itaipu-Piratininga Lake	Rio de Janeiro, Brazil	368	(Cunha et al. 2020)
Sinos River Basin	Rio Grande do Sul, Brazil	517	(Peteffi et al. 2019)
Caldas River	Sergipe, Brazil	43	(Maynard et al. 2019)
Brilhante River	Mato Grosso do Sul, Brazil	48	(Sposito et al. 2018)
Dourados River		21	
Velhas River	Minas Gerais, Brazil	198	(Weber et al. 2017)
Guarapiranga Reservoir	São Paulo, Brazil	11	(Machado et al. 2016)
Jacarepaguá River Basin	Rio de Janeiro, Brazil	39,860	(Lopes et al. 2016)
Paraíba do Sul River	São Paulo, Brazil	116.9	This study
Ganga River	India	4,460	(Chakraborty et al. 2021)
Zhujiang River	China	1,840	(Huang et al. 2020)
Dongjiang River	China	2,180	
Santa Catarina River	Mexico	30,000	(Cruz-López et al. 2020)
South Platte River	United States	150	(Bai et al. 2018)
Hogsmill River	United Kingdom	137	(Wilkinson et al. 2017)

The results showed no simple correlation between estrogenic activity and BPA concentration ($R^2 = 0.01783$), as shown in Fig. 5. A correlation analysis was also performed between BPA content and other evaluated parameters, but no simple correlation was found.

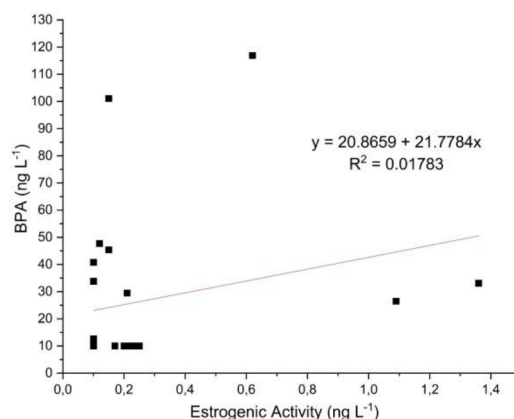


Figure 5 Linear correlation between estrogenic activity and BPA concentrations. If the result found is less than the LOQ, the LOQ value is considered

Studies have shown that BPA binding to the estrogen receptors ER α and ER β is low, with an affinity 10,000-fold lower than that of E2 for both ER types. However, it was demonstrated that BPA can elicit estrogen-like effects with the same potency as 17- β -estradiol (E2) because classical ERs interact with other transcription factors (Nadal et al. 2018). According to Nadal et al. (2018), the evidence of different pathways presented challenges the concept of BPA as a weak estrogen with no effects at low doses (1 nM). This is particularly significant because *in vivo* animal studies have demonstrated that BPA can interfere with endocrine signalling pathways at low doses during fetal, neonatal, and perinatal periods, as well as in adulthood (Alonso-Magdalena et al. 2012).

Since BPA has different action pathways than the h-ER α receptor used in estrogenic activity, it has a relative potency of only 2.26E-07 compared to E2 in the BLYES assay (Sanseverino et al. 2009). Applying this potency factor, it is possible to calculate the expected estrogenic activity as a function of the measured BPA concentration. This factor was used to BPA concentrations to calculate BPA's contribution to estrogen activity in the BLYES assay. The maximum quantified concentration of BPA (116.9 ng L⁻¹) contributed to the estrogenic activity at 2.64E-05 ng L⁻¹ of estradiol-equivalent. Compared with the 0.62 ng L⁻¹ estradiol-equivalent quantified in the BLYES assay, the BPA contribution to the BLYES assay corresponded to only 0.004% of the total estrogenic activity. The relative potency of BPA cannot fully explain the biological response, which indicates that the BLYES assay could have detected other substances, including natural and synthetic hormones found in surface water and were not chemically analyzed in this study (Di Dea Bergamasco et al. 2011).

Montagner et al. (2019) assessed the risk of surface waters using the criteria of the chronic toxicity standard, which for BPA is 240 ng.L⁻¹ (Swiss Centre for Applied

Ecotoxicology 2016), to evaluate the effects of concentration on aquatic organisms. As all the results of the Sao Paulo state stretch of Paraíba do Sul River in this study were below this criterion, it demonstrates no expected risk for water use.

Due to the importance of the Paraíba do Sul River as a water supply source in Brazil's most urbanized and industrialized states, it is necessary to continue monitoring BPA and other contaminants of emerging concern to identify other endocrine disruptors that can contribute to the levels of estrogenic activity in the Paraíba do Sul River.

Water Quality Evaluation

All results from the quality monitoring of the sites studied are presented in the supplementary material. CONAMA Resolution 357/2005 is a Brazilian law that classifies water bodies according to their uses and establishes water quality standards. According to this classification, water bodies that receive wastewater discharge should retain their characteristics and quality standards. The Paraíba do Sul River is classified as a Class 2 river (it can be used for drinking water after conventional treatment, it should protect aquatic life, and it can be used for recreation, irrigation, aquaculture, and fishing), and is expected to meet the quality standards for the multiple uses for which it is intended (CONAMA 2005).

During regular monitoring, in addition to calculating the water quality index, the parameters analysed were compared with the quality standards recommended (CETESB 2023). Figure 6 shows that most of the sites evaluated in this study presented values above the expected standard of CONAMA Resolution 357/2005 (CONAMA 2005) for *Escherichia coli* (max. 600 CFU (100 mL)⁻¹), biochemical oxygen demand (BOD) (max. 5 mg L⁻¹), total phosphorus (max. 0.1 mg L⁻¹), and dissolved oxygen (DO) (min. 5 mg L⁻¹).

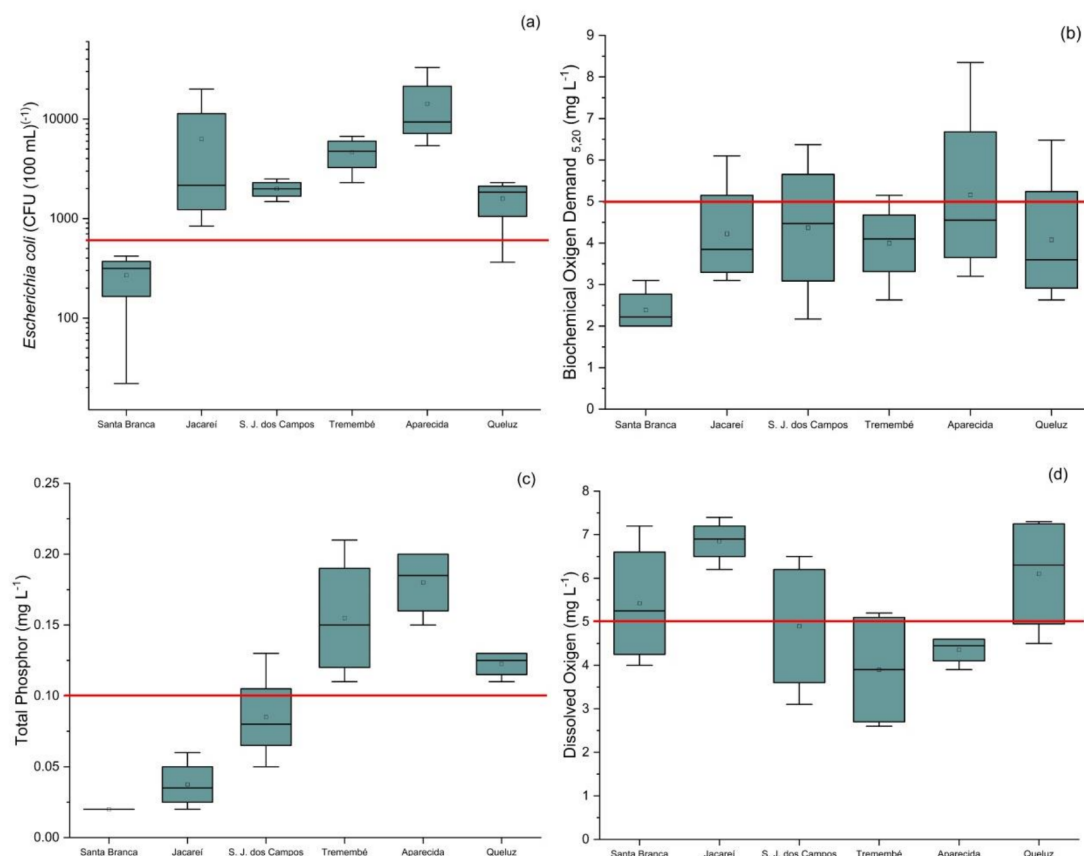


Figure 6 Comparison between the water results for *Escherichia coli* (n=24, positive n=24) (a), BOD (n=24, positive n=22) (b), total phosphorus (n=24, positive n=20) (c), and dissolved oxygen (n=24, positive n=24) (d) and the quality standards (red line) for a Class 2 river defined at CONAMA Resolution 357/2005 (CETESB 2023). The box ranges between the 25th and 75th percentiles, the whiskers show the lowest and highest values, respectively, and the horizontal bar is the median concentration.

Except for the municipality of Santa Branca, all sites showed *E. coli* results above the quality standard. The highest *E. coli* and BOD results occurred in Aparecida, which was expected because this municipality does not have a sewage treatment facility. It is possible to observe the increasing load of phosphorus along the river, with the Tremembé, Aparecida, and Queluz sites presenting all the results above the regulated quality standard. Concerning DO, the worst results occurred in the stretch between São José dos Campos and Aparecida.

These results demonstrate that releasing untreated sewage or effluents with inadequate treatment is a problem along the São Paulo stretch of the Paraíba do Sul River.

Water Quality Index

According to Chidiac et al. (2023), the water quality index (WQI) is one of the most commonly used tools for describing water quality by reducing the bulk of information (physical, chemical, and biological factors) into a single value ranging between 0 (poorer quality) and 100 (best quality). The calculated WQI for each campaign and the WQI mean value for 2022 are shown in Table 3.

Table 3 Water quality index (WQI) of the São Paulo stretch of the Paraíba do Sul River in 2022 (CETESB, 2023)

Site	Feb	May	Aug	Oct	WQI 2022
Santa Branca	67	64	78	72	70
Jacareí	57	59	67	68	63
São José dos Campos	43	55	66	63	57
Tremembé	38	54	58	47	49
Aparecida	40	50	53	45	47
Queluz	51	60	60	68	60
WQI Legend	Excellent	Good	Fair	Poor	Very Poor

February and October represent the rainy seasons, during which we observed WQI results classified as “fair”, and the Tremembé and Aparecida sites presented the worst results among all the campaigns. Comparing the WQI in 2022 with the WQI indices of the previous five years (Table S2 - supplementary material), the WQI 2022 values were lower, probably because the rainfall intensity was up to 10% greater in 2022 than the historical average (CETESB 2023).

The evaluation of the annual WQI (CETESB 2023) and BPA concentration [Figure 7 (a)], as well as the estrogenic activity [Figure 7 (b)], revealed that their highest concentrations occurred at the sites with the lowest water quality. This is explained by the river receiving more sewage downstream.

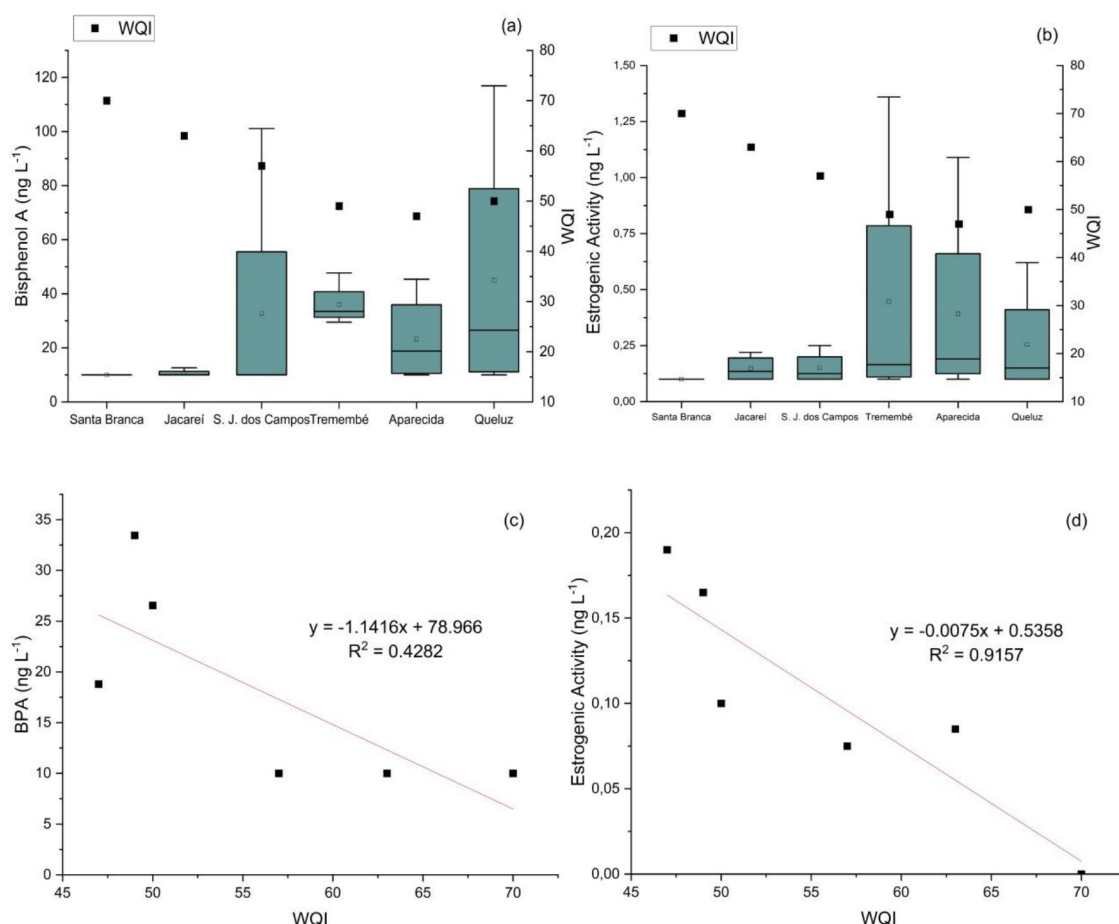


Figure 7 Comparison between the water quality index (WQI) (CETESB 2023) and the bisphenol A (a) and estrogenic activity (b) concentrations. Linear correlation between WQI and BPA mean concentrations (c) and WQI and estrogenic activity mean concentrations (d). The box ranges between the 25th and 75th percentiles, the whiskers show the lowest and highest values, respectively, and the horizontal bar is the median concentration

The linear correlation (R^2) between the WQI mean values for 2022 and the BPA and estrogenic activity mean concentrations at each site were 0.4282 and 0.9157, respectively [Figures 7 (c) and 7 (d)]. As the WQI parameters primarily indicate water body contamination from domestic sewage discharge, it is possible to infer that industrial wastewaters constitute an important share of the contributing factors to BPA contamination since the region is highly industrialized, including several chemical and petrochemical, metallurgical, paper and food industries. However, estrogenic activity is strongly correlated with inadequate disposal of domestic sewage, especially because other natural estrogens like 17β -Estradiol (E2), 17α -Ethinylestradiol (EE2), Estrone (E1), and Estriol (E2) are found in surface waters with domestic sewage contamination (Di Dea Bergamasco et al. 2011; Dias et al. 2015).

Conclusions

This study underscores the pressing issue of water pollution, mainly focusing on the emerging contaminant bisphenol A (BPA) and estrogenic activity in the Paraíba do Sul River in São Paulo, Brazil. This study quantified BPA concentrations (11.1 to 116.9 ng L⁻¹) and assessed estrogenic activity (0.12 to 1.36 ng L⁻¹ of estradiol-equivalent) using the BLYES assay, both of which showed positive results in 50% of the samples. However, the absence of a significant correlation ($R^2 = 0.01783$) between BPA concentrations and estrogenic activity suggests the presence of other compounds contributing to estrogenic effects, emphasizing the need for a comprehensive approach to monitoring water quality. Furthermore, the water quality evaluation using the water quality index (WQI) revealed compromised water quality at the studied sites, particularly during the rainy season. The correlation between the WQI and estrogenic activity ($R^2 = 0.9157$) suggested that untreated domestic sewage disposal could be an important source of endocrine-disrupting compounds. Concerning BPA contamination, its correlation with WQI ($R^2 = 0.4282$) demonstrates that it is necessary to continue studies to track the sources of pollution, especially in this highly urbanized and industrialized region. This research underscores the importance of continuous monitoring, regulatory measures, and public awareness to preserve water resources and protect public health. The findings contribute to the growing knowledge of emerging contaminants, urging decision-makers and environmental agencies to take proactive steps to safeguard water resources and public health.

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3.2 Material suplementar do artigo sobre a contaminação de BPA do rio Paraíba do Sul

Supplementary Material

Water analyses results

Site: Santa Branca

Parameter (unit)	Campaign			
	Feb-22	May-22	Aug-22	Out-22
Bisphenol A (ng L ⁻¹)	< 10	< 10	< 10	< 10
Estrogenic Activity Assay - BLYES (ng L ⁻¹)	< 0.1	< 0.1	< 0.1	< 0.1
<i>Escherichia coli</i> (CFU (100 mL ⁻¹))	324	420	22	308
pH	6.6	6.6	5.8	7.0
Biochemical Oxygen Demand (BOD) (mg L ⁻¹)	< 2	2.44	< 2	3.1
Ammonium Nitrogen (mg L ⁻¹)	< 0.5	< 0.5	< 0.5	< 0.5
Nitrate (mg L ⁻¹)	0.32	0.24	0.17	0.20
Nitrite (mg L ⁻¹)	0.01	0.02	0.02	< 0.02
Kjeldahl Nitrogen (mg L ⁻¹)	< 0.5	1.1	< 0.5	< 0.5
Total Phosphor (mg L ⁻¹)	< 0.02	0.02	< 0.02	< 0.02
Temperature (°C)	24	24	20	20
Turbidity (NTU)	18	< 5	< 5	< 5
Total Solids (mg L ⁻¹)	< 50	< 50	< 50	< 50
Dissolved Oxygen. (mg L ⁻¹)	4.5	4.0	7.2	6.0

CFU – Colony Formation Unit, NTU - Nephelometric Turbidity Unit

Site: Jacarei

Parameter (unit)	Campaign			
	Feb-22	May-22	Aug-22	Out-22
Bisphenol A (ng L ⁻¹)	12.6	< 10	< 10	< 10
Estrogenic Activity Assay - BLYES (ng L ⁻¹)	< 0.1	0.22	< 0.1	0.17
<i>Escherichia coli</i> (CFU (100 mL ⁻¹))	2,700	20,000	840	1,620
pH	7.1	7.4	6.3	7.4
Biochemical Oxygen Demand (BOD) (mg L ⁻¹)	6.1	4.2	3.1	3.49
Ammonium Nitrogen (mg L ⁻¹)	< 0.5	< 0.5	< 0.5	< 0.5
Nitrate (mg L ⁻¹)	0.29	0.30	0.19	0.23
Nitrite (mg L ⁻¹)	0.02	< 0.02	< 0.02	< 0.02
Kjeldahl Nitrogen (mg L ⁻¹)	< 0.5	< 0.5	0.64	< 0.5
Total Phosphor (mg L ⁻¹)	0.06	0.04	0.03	< 0.02
Temperature (°C)	24	24	19	20
Turbidity (NTU)	86	< 5	< 5	7
Total Solids (mg L ⁻¹)	156	98	< 50	< 50
Dissolved Oxygen. (mg L ⁻¹)	6.8	7.4	6.2	7.0

CFU – Colony Formation Unit, NTU - Nephelometric Turbidity Unit

Site: São Jose dos Campos

Parameter (unit)	Campaign			
	Feb-22	May-22	Aug-22	Out-22
Bisphenol A (ng L ⁻¹)	< 10	101.1	< 10	< 10
Estrogenic Activity Assay - BLYES (ng L ⁻¹)	< 0.1	0.15	< 0.1	0.25
<i>Escherichia coli</i> (CFU (100 mL ⁻¹))	1,480	1,880	2,500	2,100
pH	6.7	6.6	6.8	7.1
Biochemical Oxygen Demand (BOD) (mg L ⁻¹)	4	6.37	2.17	4.94
Ammonium Nitrogen (mg L ⁻¹)	< 0.5	< 0.5	< 0.5	< 0.5
Nitrate (mg L ⁻¹)	0.45	0.61	0.28	0.36
Nitrite (mg L ⁻¹)	0.012	0.03	< 0.02	< 0.02
Kjeldahl Nitrogen (mg L ⁻¹)	0.88	< 0.5	0.53	< 0.5
Total Phosphor (mg L ⁻¹)	0.08	0.13	0.05	0.08
Temperature (°C)	25	23	23	22
Turbidity (NTU)	142	< 5	< 5	12
Total Solids (mg L ⁻¹)	240	164	< 50	64
Dissolved Oxygen. (mg L ⁻¹)	3.1	4.1	6.5	5.9

CFU – Colony Formation Unit, NTU - Nephelometric Turbidity Unit

Site: Tremembe

Parameter (unit)	Campaign			
	Feb-22	May-22	Aug-22	Out-22
Bisphenol A (ng L ⁻¹)	33.8	47.7	29.5	33.1
Estrogenic Activity Assay - BLYES (ng L ⁻¹)	< 0.1	0.12	0.21	1.36
<i>Escherichia coli</i> (CFU (100 mL ⁻¹))	2,300	6,700	4,200	5,300
pH	6.1	6.9	6.4	6.8
Biochemical Oxygen Demand (BOD) (mg L ⁻¹)	4	4.2	2.63	5.17
Ammonium Nitrogen (mg L ⁻¹)	0.42	< 0.5	0.25	< 0.5
Nitrate (mg L ⁻¹)	0.66	1.38	0.63	0.81
Nitrite (mg L ⁻¹)	0.049	0.09	0.03	0.07
Kjeldahl Nitrogen (mg L ⁻¹)	1.32	3.79	0.83	< 0.5
Total Phosphor (mg L ⁻¹)	0.13	0.21	0.11	0.17
Temperature (°C)	24	24	19	23
Turbidity (NTU)	109	< 5	< 5	18
Total Solids (mg L ⁻¹)	248	110	< 50	68
Dissolved Oxygen. (mg L ⁻¹)	2.6	5.0	5.2	2.8

CFU – Colony Formation Unit, NTU - Nephelometric Turbidity Unit

Site: Aparecida

Parameter (unit)	Campaign			
	Feb-22	May-22	Aug-22	Out-22
Bisphenol A (ng L ⁻¹)	11.1	45.4	< 10	26.5
Estrogenic Activity Assay - BLYES (ng L ⁻¹)	< 0.1	0.15	0.23	1.09
<i>Escherichia coli</i> (CFU (100 mL ⁻¹))	9,800	8,900	5,400	33,000
pH	6.7	6.6	6.3	7.0
Biochemical Oxygen Demand (BOD) (mg L ⁻¹)	5	4.1	3.2	8.35
Ammonium Nitrogen (mg L ⁻¹)	< 0.5	< 0.5	0.14	< 0.5
Nitrate (mg L ⁻¹)	0.56	1.67	0.74	1.05
Nitrite (mg L ⁻¹)	0.031	0.10	0.02	0.07
Kjeldahl Nitrogen (mg L ⁻¹)	1.3	< 0.5	0.88	< 0.5
Total Phosphor (mg L ⁻¹)	0.20	0.17	0.15	0.20
Temperature (°C)	24	23	19	25
Turbidity (NTU)	210	< 5	< 5	42
Total Solids (mg L ⁻¹)	238	124	< 50	96
Dissolved Oxygen. (mg L ⁻¹)	4.3	3.9	4.6	4.6

CFU – Colony Formation Unit, NTU - Nephelometric Turbidity Unit

Site: Queluz

Parameter (unit)	Campaign			
	Feb-22	May-22	Aug-22	Out-22
Bisphenol A (ng L ⁻¹)	12.3	40.8	< 10	116.9
Estrogenic Activity Assay - BLYES (ng L ⁻¹)	< 0.1	< 0.1	0.2	0.62
<i>Escherichia coli</i> (CFU (100 mL ⁻¹))	1,940	1,740	2,300	364
pH	6.8	6.9	6.3	7.0
Biochemical Oxygen Demand (BOD) (mg L ⁻¹)	4	3.2	2.63	6.48
Ammonium Nitrogen (mg L ⁻¹)	0.12	< 0.5	< 0.1	< 0.5
Nitrate (mg L ⁻¹)	0.41	1.75	0.90	1.51
Nitrite (mg L ⁻¹)	0.015	0.08	0.02	0.08
Kjeldahl Nitrogen (mg L ⁻¹)	1.13	< 0.5	0.89	< 0.5
Total Phosphor (mg L ⁻¹)	0.13	0.11	0.13	0.12
Temperature (°C)	24	24	21	26
Turbidity (NTU)	292	< 5	< 5	14
Total Solids (mg L ⁻¹)	230	52	< 50	< 50
Dissolved Oxygen. (mg L ⁻¹)	7.2	4.5	5.4	7.3

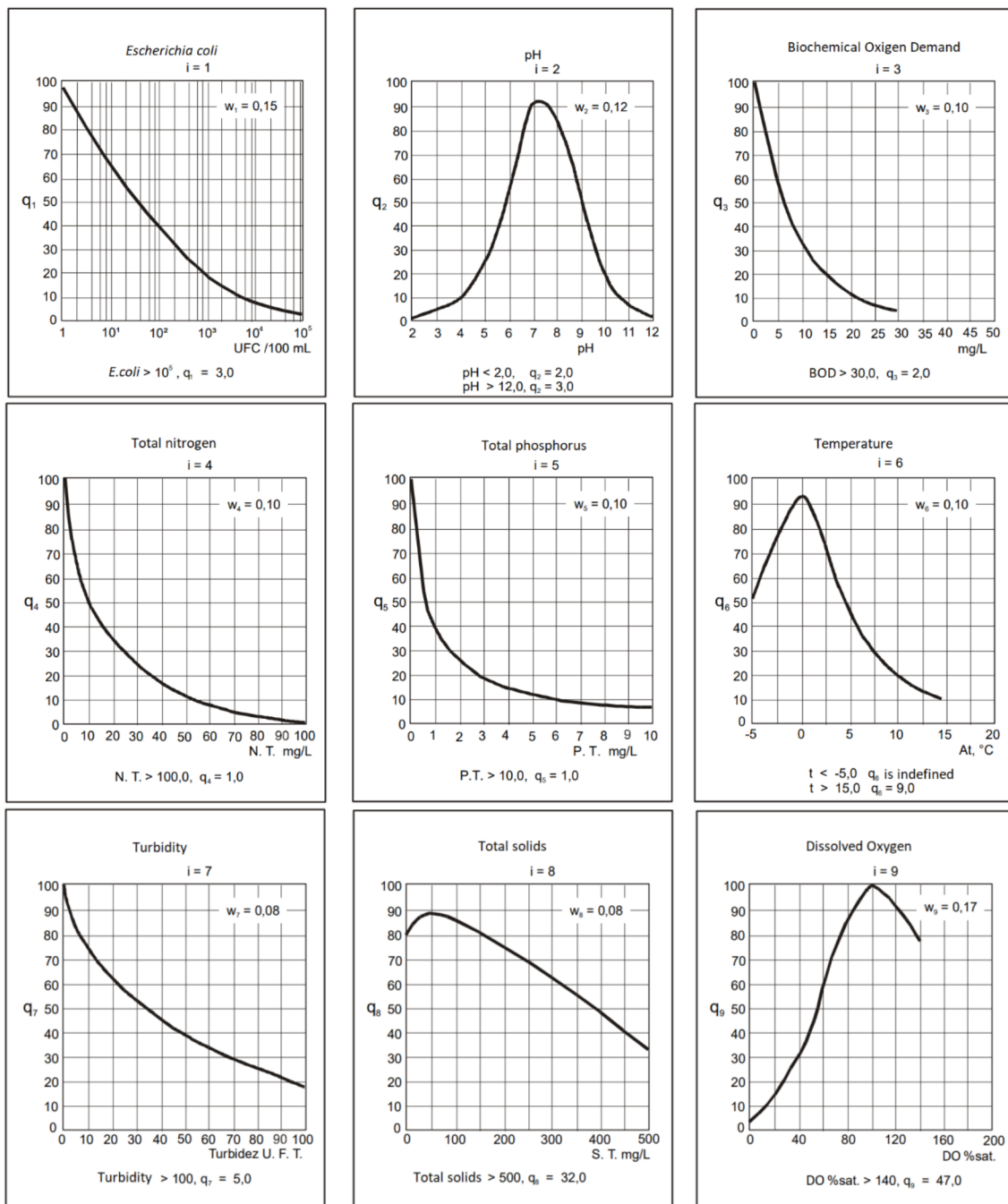
CFU – Colony Formation Unit, NTU - Nephelometric Turbidity Unit

Water analyses methods

Parameter	Analyses Methods
Bisphenol A	Described at material and methods.
Estrogenic Activity Assay - BLYES	Described at material and methods.
<i>Escherichia coli</i>	(U.S. EPA 2014) - Method 1603
pH	(APHA 2023) – Method 4500-H ⁺ B – Eletrometric method
Biochemical Oxygen Demand (BOD)	(APHA 2023) – Method 5210 B – 5 Day BOD Test
Ammonium Nitrogen	(APHA 2023) – Method 4500-NH ₃
Nitrate	(APHA 2023) – Method 4500-NO ₃
Nitrite	(APHA 2023) – Method 4500-NO ₂
Kjeldahl Nitrogen	(APHA 2023) – Method 4500-N _{org}
Total Phosphor	(US EPA 2018) – Method 6010D
Temperature	(APHA 2023) – Method 2550 B
Turbidity	(APHA 2023) – Method 2130 B – Nephelometric Method
Total Solids	(APHA 2023) – Method 2540 B – Total solids dried from 103 to 105 °C.
Dissolved Oxygen.	(APHA 2023) – Method 4500-O G – Membrane-Electrode Method.

Water Quality Index

Figure S1 – Average Water Quality Variation Curves (CETESB 2023)



The ratings of WQI are defined in the following table.

Table S1. Colors and definition used in the classification of WQI

Color	The numerical value index	Definition
Purple	$WQI \leq 19$	Very Poor
Red	$19 < WQI \leq 36$	Poor
Yellow	$36 < WQI \leq 51$	Fair
Green	$51 < WQI \leq 79$	Good
Blue	$79 < WQI \leq 100$	Excellent

Table S2. Annual water quality index of the São Paulo stretch of the Paraíba do Sul River from 2017 to 2022 (CETESB 2023)

Site	2017	2018	2019	2020*	2021	2022
Santa Branca	71	73	70	-	72	70
Jacareí	62	65	67	-	67	63
São José dos Campos	61	62	60	60	57	57
Tremembé	59	58	57	-	56	49
Aparecida	51	50	49	53	51	47
Queluz	64	62	61	60	57	60

WQI Legend	Excellent	Good	Fair	Poor	Very Poor
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* During the Coronavirus pandemic, the water quality monitoring program was shortened, and not all the sites were evaluated.

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4 ARTIGO SOBRE O ADSORVENTE DESENVOLVIDO

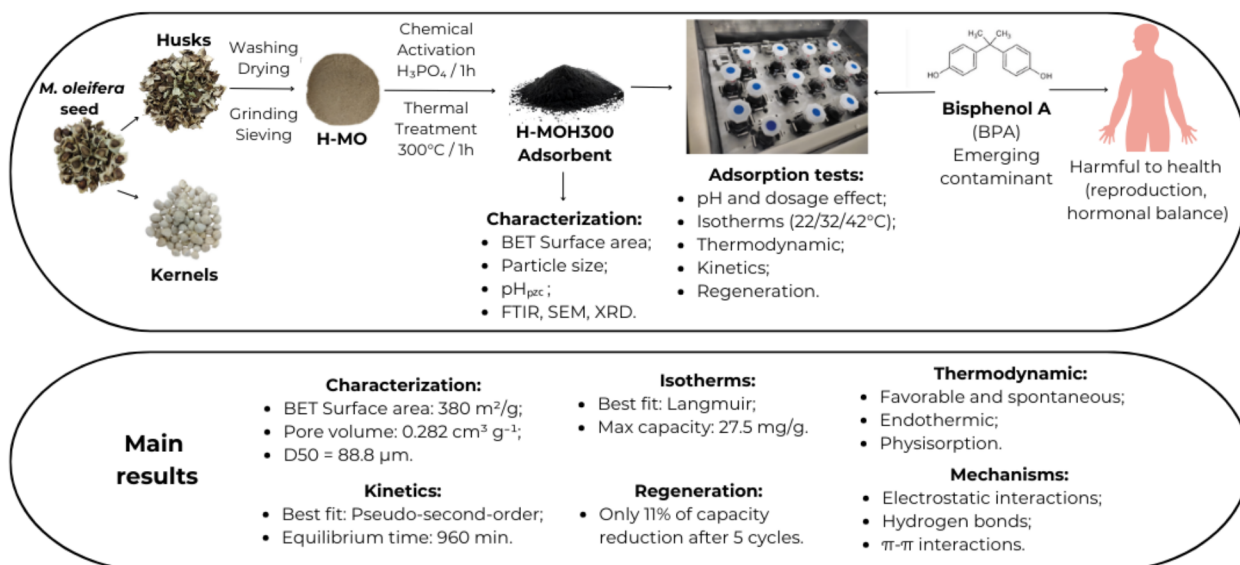
4.1 Emerging contaminant bisphenol A removal from water via modified *Moringa oleifera* seed husk biomass as an eco-friendly adsorbent

ABSTRACT

Bisphenol A (BPA), a commonly used chemical for producing plastics and epoxy resins, has been found in surface waters. BPA is a contaminant of emerging concern due to its harmful effects on human and animal health, including impacts on reproduction and hormonal balance. The utilization of *Moringa oleifera* seeds results in the generation of husks as a residue. This study investigated BPA removal from water via the use of modified *M. oleifera* seed husks (H-MOH300) as an eco-friendly adsorbent. The seed husks were chemically activated with phosphoric acid and thermally treated at 300°C. The activation process resulted in a material with a BET-specific surface area of 380 m² g⁻¹ and a total pore volume of 0.282 cm³ g⁻¹. The Langmuir isotherm model described the adsorption process most accurately, with a maximum adsorption capacity of 27.5 mg g⁻¹ at 22°C. Thermodynamic analysis indicated that the adsorption was spontaneous, endothermic, and primarily driven by electrostatic and π - π interactions. Regeneration studies indicated that H-MOH300 could be effectively reused, suggesting its potential as a sustainable adsorbent for BPA removal. This work highlights the utility of agricultural waste materials for environmental remediation, providing a cost-effective solution for treating water contaminated by emerging pollutants such as BPA.

Keywords: adsorption, BPA, contaminants of emerging concern, endocrine disruptor, low-cost adsorbent

GRAPHICAL ABSTRACT



1. INTRODUCTION

The substance 2,2-bis(4-hydroxyphenyl) propane, commonly known as bisphenol A (BPA), is frequently used to produce epoxy resins and polycarbonate plastics. BPA is also used in the industrial manufacturing of plastic bottles, can linings, and thermal papers [1]. Many studies have highlighted the harmful effects of BPA, including its impact on reproduction, genetics, the nervous system, embryo development, and hormonal balance [2,3]. Studies have shown worldwide BPA contamination in freshwaters used as sources of drinking water after treatment, especially in the most industrialized and urbanized regions [4–7]. Considering that the conventional drinking water treatment process, which involves coagulation, flocculation, sedimentation, and filtration stages, has low BPA removal rates [8,9] and is the most applied process worldwide [10], developing alternative treatments for BPA removal from water is imperative.

Various methods for removing BPA from water, including membrane filtration, biological processes, ultraviolet (UV) irradiation, and advanced oxidation techniques, have been investigated. However, challenges such as high cost and energy consumption, low process efficiency, the generation of toxic by-products, and the use of hazardous chemicals limit the widespread implementation of these technologies on a large scale [11,12].

Adsorption is also considered an effective method for BPA removal. However, large-scale application of commercial activated carbons is still a challenge because of their high costs for activation related to energy consumption ($500\text{--}900\text{ }^\circ C$) [12]. To address

these challenges, increasing attention has been given to developing and producing environmentally friendly adsorbents using low-cost agricultural waste materials.

The utilization of agricultural waste materials as adsorbents to eliminate BPA has garnered significant attention. This is due to their abundance in nature, diverse functional groups, eco-friendliness, low cost, ease of surface modification, chemical stability, renewability, and biodegradability. These qualities make them favourable for regeneration and reuse after adsorption [12,13]. Therefore, developing new low-cost and eco-friendly adsorbents to remove BPA from water is essential.

Moringa oleifera (MO) is a plant belonging to the *Moringaceae* family that is native to India and the sub-Himalayan regions. MO is now commonly found in tropical areas, including the American continent [14]. In addition to the various applications of MO as a food and medicinal plant, MO seeds have been used as a natural coagulant in water and wastewater treatment [15–17]. However, the use of MO seeds generates husks as waste, which have been studied for potential applications as adsorbents for different contaminants, such as methylene blue [18], atrazine [19], and acetaminophen [20]. However, no studies in the literature have reported the potential use of MO seed husks as an adsorbent for bisphenol A (BPA) removal. Furthermore, research using MO husks as adsorbents indicates a low surface area post-activation, with surface areas such as 4.6 m²/g [20] and 10.32 m²/g [19]. Further studies are needed to enhance this crucial property for effective adsorption [21].

In this context, considering the need to develop low-cost and eco-friendly adsorbents for removing BPA from water due to associated risks to human health and the environment and the need to address the residue (husks) from MO seeds, this study aims to evaluate the optimal activation method for MO seed husks and their use as a sustainable adsorbent for BPA removal, which is a novel contribution to contaminant water removal. This work presents a systematic investigation, including adsorbent characterization, equilibrium, kinetics, thermodynamics, adsorption mechanism, and regeneration process studies.

2. MATERIALS AND METHODS

2.1. Adsorbent Preparation

Moringa oleifera seeds (purchased from Arbocenter, Brazil) were manually peeled, and the seed husks were dried at 105°C for 2 h. After drying, the husks were ground and sifted to

be standardized to a 28-mesh (600 μm) maximum particle size. The obtained powder was used as an adsorbent (H-MO) and was also the precursor for the chemically and thermally treated adsorbents.

Chemical activation (CA) was carried out via potassium hydroxide (KOH) (purity 85%, ACS Científica) or phosphoric acid (H_3PO_4) (purity 85%, Vetec), as these reagents have shown promising results in activating precursors from agricultural waste to remove BPA [1,2,3,4]. CA occurred at a mass ratio of 1:5 m/v (H-MO/KOH or H_3PO_4) in aqueous solution (0.1 mol L^{-1}), which was maintained for 1 h at room temperature and then dried at 105°C for 15 h. The chemically activated material was subsequently thermally activated in a single stage (carbonization and activation) in a muffle furnace (LF02310, Jung) at a heating rate of $20^\circ\text{C min}^{-1}$ under two different conditions (300°C or 500°C) for one hour. The mixture was then washed with deionized water until a neutral pH was reached. Only thermal activation of H-MO at 750°C for 30 min (H-MO750) was also carried out. A summary of the chemical and physical activations is presented in Table 1. After preliminary adsorption tests, the most promising material was chosen for the study.

2.2. Characterisation

The adsorbent was characterized by scanning electron microscopy (SEM) (FEI model INSPECT S50 equipment) to determine the surface morphology, N_2 physisorption (BET) (NOVA 4200e, Quantachrom) to determine the specific surface area, Fourier transform infrared spectroscopy (FTIR) (IR PRESTIGE-21, Shimadzu) operating in the attenuated total reflectance (ATR) mode to determine the surface functional groups, X-ray diffraction analysis (XRD) (Miniflex 600, Rigaku) to evaluate the structural properties, and multi-laser technology to determine the particle size distribution (CILAS 1190, CPS US, Inc.).

The point of zero charge (pH_{PZC}) test was performed via the salt addition method with NaNO_3 (purity $\geq 98\%$, Êxodo Científica) in an aqueous solution (0.1 mol L^{-1}) according to Bakatula et al. [23]. In the ‘11 point experiment’ method, 50 mL of NaNO_3 solution at different initial pH values (2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12) adjusted with HCl (purity = 36.80%, Neon) (0.1 mol L^{-1}) or NaOH (purity = 98.81%, Neon) (0.1 mol L^{-1}) was added to 0.2 g of sample, which was shaken on a temperature-controlled stirring apparatus (Dubnoff 304-TPA) at 100 rpm and 22°C for 16 h.

2.3. Adsorption studies

Preliminary adsorption tests were conducted with the adsorbents H-MO, H-MO 750, H-MOK300, H-MOK500, and H-MOH300 in the batch adsorption process using a 2 g L⁻¹ dosage of the adsorbent in 50 mL of BPA (purity ≥ 99%, Sigma–Aldrich) solution with a 20 mg L⁻¹ concentration for 24 h at room temperature to evaluate the most promising candidate for BPA removal. BPA quantification was performed with a UV–Vis spectrophotometer (Genesys 50, Thermo Fisher Scientific) at 276 nm. The parameters of the BPA analysis method are described in the supporting information.

The adsorption tests were carried out in batch mode in triplicate via a temperature-controlled stirring apparatus (Dubnoff 304-TPA) at 100 rpm at room temperature for 24 h. The adsorbent dosage effect was evaluated using 0.6, 1.0, 1.6, 2.0, 3.0, 4.0, 5.0, and 6.0 g L⁻¹ adsorbent in 50 mL of BPA (20 mg L⁻¹) at a pH of 6.0. To evaluate the effect of the pH, 2.0 g L⁻¹ adsorbent and 50 mL of BPA (20 mg L⁻¹) solution were used, and the pH was adjusted to 5, 6, 7, 8, 9, 10, 11, 12, and 13.

2.4. Adsorption kinetics

The kinetic study was conducted under the optimal conditions, with 2.0 g L⁻¹ adsorbent in 50 mL of BPA solution (20 mg L⁻¹). The contact time intervals from the analysed samples were 0.5–32 h at a temperature of 22°C at 100 rpm. After the contact time, the solutions were filtered through a Whatman filter n° 1, and the BPA concentration was quantified. The data were subjected to nonlinear regression analysis via the OriginPro® 2024 software program. The adsorption capacity q (mg g⁻¹) was calculated and the equation is presented in the supporting information.

Kinetic studies were conducted via the pseudo-first-order (PFO) equation proposed by Lagergren [24], the pseudo-second-order (PSO) equation proposed by Ho and Mckay [25], the intraparticle diffusion equation proposed by Weber and Morris [26], and the Elovich equation proposed by McLintock [27]. The kinetic equations are expressed in the supporting information.

2.5. Adsorption isotherms

Three different temperatures (22°C, 32°C, and 42°C) were used to determine the adsorption equilibrium of BPA and the effect of temperature. A BPA concentration of 10–

120 mg L⁻¹ was studied in 50 mL of solution, with 2.0 g L⁻¹ adsorbent, a contact time of 16 h, a pH of 6.0, and a stirring speed of 100 rpm. After the conclusion of the contact time, the BPA concentration was analysed.

This study tested the Langmuir, Freundlich, and Temkin isotherm models via nonlinear regression analysis. The Langmuir isotherm assumes a finite number of independent active sites, with no interaction or competition between them. The adsorption probability at an active site remains unaffected by the occupation of neighbouring sites [28]. The Freundlich model is related to heterogeneous surfaces and does not make assumptions about the adsorption capacity of the monolayer. Instead, it assumes that adsorbed molecules interact [29]. The Temkin and Pyzhev model assumes that the process heat decreases linearly as the surface layers of the solid increase [30]. The Langmuir, Freundlich, and Temkin equations are presented in the supporting information.

2.6. Thermodynamics

Thermodynamic studies are indispensable for understanding adsorption mechanisms [31]. On the basis of the equilibrium adsorption experimental data, the thermodynamic parameters can be calculated according to thermodynamic laws. The Gibbs free energy (ΔG°) (kJ mol⁻¹) was estimated according to Equation (1).

$$\Delta G^\circ = -RT \ln K_C \quad (1)$$

The relationships among ΔG° , enthalpy (ΔH°) (kJ mol⁻¹) and entropy (ΔS°) (J mol⁻¹ K⁻¹) are described in Equation (2), and the van't Hoff Equation (3) is obtained by substituting Equation (1) into Equation (2).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

$$\ln K_C = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (3)$$

where R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the temperature in K.

K_C should be dimensionless and was obtained by multiplying K_L by the molecular weight of the adsorbate (M_w) (g mol⁻¹), by 1,000, and then by 55.5 (Equation (4)) [32].

$$K_C = M_w \times 55.5 \times 1,000 \times K_L \quad (4)$$

2.7. *Regeneration study*

To investigate the reusability of the adsorbent, an adsorption test was carried out with 250 mL of BPA solution (120 mg L^{-1}) and 2.0 g L^{-1} adsorbent at 22°C for 16 h. The loaded adsorbent was filtered and washed thoroughly with deionized water. It was then introduced into 50 mL of ethanol solution (75% v/v) (purity 95.1–96.9%, Merck) and stirred at 100 rpm for 5 h. Ethanol was chosen because it was shown to be a proper substance for BPA desorption from other adsorbents [13,14,33]. The regenerated adsorbent was filtered, washed thoroughly with deionized water, and dried at 105°C for 1 h. Five adsorption–desorption cycles were carried out in triplicate, and the adsorption capacity q (mg g^{-1}) was measured after each cycle.

3. RESULTS AND DISCUSSION

3.1. *Activation performance*

The five types of adsorbents produced were preliminarily tested in the batch adsorption process. The efficiency of BPA removal in preliminary tests and the yield rate were calculated and are shown in Table 2. The H-MOH300 adsorbent was selected for this study on the basis of its ability to remove BPA from aqueous solution (67% removal and an adsorption capacity of 6.6 mg g^{-1}) and its production yield (26%) compared with those of the other adsorbents studied.

3.2. *Characterization*

3.2.1. *BET analysis and particle size distribution*

The N_2 adsorption–desorption curves of the H-MOH300 adsorbent are presented in Figure 1, which shows the behaviour of a reversible type II isotherm. This type of isotherm is typical of a macroporous material with gradual curvature related to monolayer coverage (point B), indicating multilayer adsorption [33]. The hysteresis loop is type H3, which is characteristic of nonrigid aggregates of plate-like particles, despite desorption not converging to adsorption. The curves for adsorption/desorption do not overlap, possibly because N_2 might have been trapped between the plates or fibres, and at P/P_0 values below 0.5, the cavitation process forced out N_2 .

H-MOH300 presented a BET specific surface area and total pore volume of $380 \text{ m}^2 \text{ g}^{-1}$ and $0.282 \text{ cm}^3 \text{ g}^{-1}$, respectively. Compared with those of H-MO, the specific surface area and porosity of H-MO increased after chemical and thermal treatment, which presented a surface area and total pore volume of $3.24 \text{ m}^2 \text{ g}^{-1}$ and $0.010 \text{ cm}^3 \text{ g}^{-1}$, respectively [18]. Compared with other studies with modified MO husks, the BET specific surface area of H-MOH300 substantially increased (Table 3). This can be associated with the method of preparation of the adsorbent. Quesada et al. [20] prepared an adsorbent from MO seed husk modified with phosphoric acid at 300°C . However, the precursor was washed before the heating process, unlike the H-MO used in this study, which was washed only after thermal activation. The presence of phosphoric acid during thermal activation may explain the larger surface area of H-MOH300. In their research, chemical activation was performed with a ratio of 30 g to 1 L of 0.1 mol L^{-1} phosphoric acid for 3 h, whereas H-MOH300 was activated with a 1:5 (m/v) ratio for 1 h. Another difference to be considered is the separation by particle size; they used particles between 500 and 600 μm [20], and the particle size distribution of H-MOH300 is from 0.04 μm to 600 μm , with an 88.8 μm D50 and 294.2 μm D90 (Figure 2). These differences could explain the difference in the BET specific surface area between the two adsorbents, especially the particle size, since a study with BPA adsorption showed that as the particle size increased, the sorption capacity decreased [34].

3.2.2. Surface morphology and crystallinity

The SEM image (Figure 3) shows heterogeneous morphological characteristics, and the porous and fibrous structures presented agree with previous observations [19,20,35]. The surface presents some pores that are $4.06 \pm 1.62 \text{ }\mu\text{m}$ in size connected to the inside of the fibres, which explains the isotherm type and lack of overlap of N_2 desorption (Figure 1).

The X-ray diffractogram presented in Figure 4 shows a defined peak at $2\theta = 25^\circ$, indicating the presence of an alignment of the material layers [35]. An elevation is also observed at $2\theta = 45^\circ$. It cannot be considered a peak, but its presence can be explained by the heterogeneity and complexity of the adsorbent [35]. This elevation could be associated with disordered layers of graphite formed during the activation process [36].

3.2.3. FTIR spectroscopy

The Fourier transform infrared spectra are shown in Figure 5, in which the functional groups present in H-MOH300 were determined before and after BPA adsorption. The broad peak at 3342 cm^{-1} indicates the presence of O–H hydroxyl bonds [20,38,39]. The band at 1589 cm^{-1} indicates the presence of aromatic rings [20]. Furthermore, the peak at 1232 cm^{-1} is associated with C–O groups [20], which, along with the O–H band, may indicate the presence of carboxylic functional groups. After BPA adsorption, additional peaks related to BPA molecules can be observed. The peak at 2980 cm^{-1} is possibly associated with C–H bonds. The peak at 1508 cm^{-1} is related to H–C–H interactions outside the aromatic rings; the peak at 829 cm^{-1} could be related to C–O stretching and C–C stretching in both the rings and from C–H out-of-plane bending movements. In addition, the peak at 746 cm^{-1} could be caused by C–C stretching in BPA molecules [40].

3.2.4. Point of zero charge (pH_{PZC}) and the effect of the pH on the adsorption process

The pH_{PZC} analysis of H-MOH300 is shown in Figure 6. The pH_{PZC} of approximately 4.5 is the neutral loading point of H-MOH300. The pH_{PZC} value is important to consider when studying the adsorption process. If the solution pH exceeds the pH_{PZC} value, the functional groups of the adsorbent become deprotonated, leading to a negatively charged surface, which enhances the adsorption of cationic adsorbates [18]. For H-MOH300, deprotonation is favoured due to the low pH_{PZC} value, indicating that the protons are weakly bonded to the functional groups. This is because the driving force in the solution, which is composed of anionic groups such as OH^- and NO_3^- , is strong enough to eliminate them. At pH values below the pH_{PZC} , the positive charge developed on the adsorbent surface is smaller than that at pH values above the pH_{PZC} . This suggests that the functional groups responsible for increasing the pH are more strongly bonded to the adsorbent surface and that the driving force of the solution (e.g., H^+ and Na^+) cannot displace them. This observation is consistent with the FTIR results (Figure 5), which indicate the presence of carboxylic groups and explain the pH_{PZC} profile.

The pK_a values of BPA range from 9.6–10.2 [41,42]. This means that when the pH is higher than the pK_a , the BPA molecule can undergo ionization to form a bisphenol anion. This leads to electrostatic repulsion between the negatively charged carbon surface and the bisphenol anion, which reduces the adsorption of BPA onto the adsorbent. However, when the pH is lower than the pK_a , BPA adsorption remains at its highest level and nearly constant because BPA is undissociated. At this pH, the adsorptive interaction

between the undissociated BPA molecules and the adsorbent is the main factor [42]. Figure 7 shows the results for the pH effect. The significant reduction in adsorption capacity at pH values exceeding 8.2 can be attributed to electrostatic repulsion. This repulsion arises from the negative charges on the surface of the adsorbent, which has a pH_{PZC} of 4.5, and BPA, which has a pK_a ranging between 9.6 and 10.2. At higher pH values, the adsorbent and BPA molecules become negatively charged, resulting in repulsive interactions that hinder effective adsorption. Considering that tests with pH values between 5.9 and 6.6 presented approximately the same q_e , a pH of 6 was chosen for the subsequent experiments since there was no need for pH correction.

3.3. Adsorption studies

3.3.1. Adsorbent dosage effect on the adsorption capacity

The effect of the H-MOH300 concentration on the capacity for BPA adsorption is shown in Figure 8. At initial concentrations, the percentage of BPA removal increases sharply as the adsorbent dosage increases. This increase could be linked to the greater quantity of active adsorption sites available on the adsorbent [13]. The adsorption capacity values (q_e) decreased as the H-MOH300 concentration increased. This can be attributed to the larger quantity and greater availability of binding sites as the adsorbent mass increases. As a result, determining the maximum adsorption capacity is not possible because the remaining sites are not saturated [20]. The maximum removal of $74 \pm 2\%$ was achieved at a dosage of 3 g L^{-1} . At a dosage of 2 g L^{-1} , a BPA removal efficiency of $69 \pm 3\%$ was attained, and further increasing the dosage did not significantly improve the removal efficiency. Therefore, using 2 g L^{-1} adsorbent is economically justified and was selected for this study.

3.3.2. Adsorption isotherms

Figure 9 shows the experimental data obtained at 22°C , 32°C , and 42°C by plotting the BPA adsorbed on H-MOH300 at equilibrium (q_e) versus the equilibrium BPA concentration in solution (C_e). The maximum adsorption capacity improved with increasing temperature. The isotherm equations provide the parameters outlined in Table 4. Furthermore, the suitability of these equations was assessed via the most suitable statistical parameters (R^2 and χ^2) for equilibrium curves.

On the basis of the information in Table 4, the Langmuir model provided the best fit for the three temperatures tested (higher R^2 and lower χ^2). This suggests that the

adsorption surface is uniform, that the adsorption takes place at specific locations, and that the maximum adsorption indicates saturation of the monolayer [35]. Table 5 shows the comparative effectiveness of H-MOH300 with other adsorbents previously used for BPA removal from contaminated water sources. H-MOH300 demonstrated a higher adsorption capacity than other natural adsorbents did.

3.3.3. Thermodynamic study

Studying the thermodynamic process of adsorption is important for understanding how adsorption works and whether adsorption is through physical or chemical mechanisms. Specific thermodynamic parameters, such as the change in Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), can distinguish physical from chemical adsorption [45]. As the experimental equilibrium data (Figure 9) indicated a dependence on temperature, the thermodynamic parameters of the BPA adsorption process onto H-MOH300 were investigated via the Langmuir model, which best fitted the experimental data. Table 6 lists the calculated values of ΔG° , ΔH° , and ΔS° . The parameter K_C was calculated using the K_L constant from the Langmuir model via Equation (4).

The change in Gibbs energy is crucial in deciding how spontaneous the adsorption process is. If the Gibbs energy is negative, the adsorption process will occur favourably and spontaneously at a given temperature [45], as presented for H-MOH300. The Gibbs energy also decreases with increasing temperature, which implies that BPA removal is favoured with increasing heat. The positive enthalpy shows that the BPA adsorption process with H-MOH300 absorbs heat, making it an endothermic process. An enthalpy of less than 20 kJ mol^{-1} indicates physisorption [46]. The positive entropy value suggests that the organization of the adsorbate at the solid/solution interface becomes more random, indicating a dissociative mechanism. Other authors have also reported that the adsorption of BPA is endothermic, with an enthalpy value indicating physisorption and positive values for the change in entropy (ΔS°) [13,47].

3.3.4. Adsorption kinetics

The kinetics of the adsorption data were analysed via the pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich kinetic models. The results are illustrated in Figure 10, and the corresponding parameters are provided in Table 7. The adsorption capacity of H-MOH300 for BPA increases and becomes stable with a contact time of 960 min ($q_e = 8.20 \text{ mg g}^{-1}$). On the basis of the regression coefficients R^2 , error function

analyses (χ^2), and proximity of the experimentally determined q_t values to the theoretical values, the pseudo-second-order kinetic model was clearly preferable, indicating that physical interactions occurred between the adsorbent and adsorbate [48]. This model also accurately represents the kinetics data for other BPA adsorption processes [38,39,47].

3.4. Mechanisms of adsorption

On the basis of the dataset discussed, BPA removal by H-MOH300 primarily occurs through electrostatic interactions. This is supported by the increased adsorption capacity at pH values above the pH_{PZC} and below the BPA pK_a . At a pH of 6, the adsorbent surface is partially negative, as indicated by the pH_{PZC} profile (Figure 6), suggesting the presence of both protonated and nonprotonated functional groups. According to the FTIR analysis after adsorption (Figure 5), the O–H functional groups were not suppressed, and C–O and H–C–H functional groups were observed. The electrostatic potential map of BPA [49] indicates that the carbons in the ring are likely bonded to both nonprotonated and protonated adsorbent surface groups, whereas the oxygen atoms are bound to protonated groups and to the hydrogen of the OH functional group of BPA. The proposed interaction between BPA and H-MOH300 is illustrated in Figure 11. Other authors have reported similar conclusions regarding the adsorption of BPA by agricultural waste adsorbents [38,50,51]. The calculated ΔH° ($2.9128 \text{ kJ mol}^{-1}$) also supports the hypothesis that these interactions are primarily electrostatic, indicative of physisorption with no electron sharing or exchange. On the basis of the FTIR spectra (Figure 5), the O–H groups of H-MOH300 could interact with BPA molecules through dipole–dipole hydrogen bonds, and the aromatic rings in both H-MOH300 and BPA structures can also favour π – π interactions [33].

3.5. Regeneration study

The regeneration capacity of an adsorbent corroborates its effectiveness, stability, and reusability for adsorption, as well as its economic feasibility [14]. Figure 12 shows the H-MOH300 regeneration capacity for BPA adsorption after five cycles. The adsorption capacity of H-MOH300 decreases by approximately 11% over the cycles, ranging from 22.5 to 20.1 mg g^{-1} . These results demonstrated the capacity of H-MOH300 to be restored and utilized multiple times in water treatment processes, similar to other adsorbents investigated for BPA removal in the recent literature [47][13][14].

4. CONCLUSIONS

This research assessed the bisphenol A (BPA) adsorption capacity of an adsorbent prepared with *Moringa oleifera* seed husks chemically activated with phosphoric acid and thermally activated at 300°C. The BET-specific surface area and total pore volume of 380 m² g⁻¹ and 0.282 cm³ g⁻¹, respectively, indicate successful activation compared with the *M. oleifera* seed husk activation reported in the literature. The Langmuir model isotherm provided the best fit for the three temperatures tested, indicating a favourable adsorption process with a maximum adsorption capacity of 27.5 ± 1.3 mg g⁻¹ at 22°C, which is higher than that reported in some agricultural waste adsorbent studies on the removal of BPA recently published in the literature. The adsorption process is endothermic, with a ΔH° of 2.9 kJ mol⁻¹, indicating physisorption. The adsorption process is also spontaneous, with a ΔG° ranging from -35.1 to -32.7 kJ mol⁻¹. The results also suggest that the adsorption mechanisms are mainly electrostatic, with some hydrogen bonds and π - π interactions. H-MOH300 presented a good regeneration capacity after five adsorption-desorption cycles, making it a promising adsorbent for BPA removal in aqueous solutions. Since seed husks are considered agricultural waste, their use as adsorbents is a promising, low-cost solution that can minimize the environmental consequences of their improper disposal.

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Tables

Table 1. Chemical and physical activations using *M. oleifera* seed husk powder as a precursor.

Adsorbent	Chemical activation	Physical activation
H-MO	-	-
H-MO750	-	750°C/30 min
H-MOK300	KOH/60 min	300°C/60 min
H-MOK500	KOH/60 min	500°C/60 min
H-MOH300	H ₃ PO ₄ /60 min	300°C/60 min

Table 2. Adsorption of BPA by different adsorbents derived from H-MO with different chemical and thermal activations.

Adsorbent	q (mg g ⁻¹)	BPA Removal %	Yield rate %
H-MO	0	0	83.9
H-MO750	0	0	1.5
H-MOK300	0	0	10.8
H-MOK500	2.3	15.5	2.1
H-MOH300	6.6	66.6	25.6

Table 3. BET specific surface areas of different modified *Moringa oleifera* seed husk adsorbents.

Modification Method	BET specific surface área (m ² g ⁻¹)	Reference
-	3.24	[18]
H ₃ PO ₄ at 300°C	4.6	[20]
Methylic alcohol, HNO ₃ at 300°C	5.77	[35]
Methylic alcohol, HNO ₃ at 300°C	10.32	[19]
H ₃ PO ₄ at 300°C	380	This study

Table 4. Isotherm model parameters of equilibrium adsorption data for BPA onto H-MOH300.

Isotherm Model	Parameters	22°C	32°C	42°C
Langmuir	$q_{\text{máx}}$ (mg g ⁻¹)	27.5 ± 1.3	27.9 ± 1.6	32.7 ± 1.8
	K_L (L mg ⁻¹)	0.048 ± 0.006	0.049 ± 0.008	0.052 ± 0.007
	R^2	0.9815	0.9690	0.9727
	χ^2	0.7359	1.2245	1.3185
Freundlich	K_F (mg g ⁻¹)	3.1 ± 0.5	3.2 ± 0.6	3.8 ± 0.5
	n	2.1 ± 0.2	2.2 ± 0.2	2.1 ± 0.2
	R^2	0.9509	0.9339	0.9660
	χ^2	1.9494	2.6133	1.6395
Temkin	K_T (L mg ⁻¹)	0.53 ± 0.07	0.50 ± 0.07	0.57 ± 0.08
	b_T (J mol ⁻¹)	419 ± 22	416 ± 22	376 ± 22
	R^2	0.9709	0.9691	0.9639
	χ^2	1.1567	1.2220	1.7411

Table 5. Comparison of the maximum adsorption capacity of adsorbents from different sources for BPA.

Absorbents	Modification Method	Temperature (°C)	$q_{\max}$ (mg g ⁻¹)	Reference
<i>MO</i> pods	ZnCl ₂ at 500°C	25	20.14	[39]
Barley husk	HCl, dried at 105°C	25	15.51	[43]
Cellulose fibres- Spanishbroom plant (FF)	Hydrophobization with MDI	20	4.86	[11]
Rice husk ash	-		2.65	[44]
Reed straws	K ₃ PO ₄ at 500°C	25	1.72	[38]
<i>MO</i> husk seed	H ₃ PO ₄ at 300°C	22	27.5	This study

Table 6. Thermodynamic parameters of BPA adsorption using H-MOH300 as the adsorbent.

Temperature (°C)	K_C	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	Van't Hoff equation
22	611,965	-32.7	2.9	120.6	Y=-350.3x+14.5 R ² = 0.93
32	624,635	-33.9			
42	660,111	-35.1			

Table 7. Kinetic model parameters for BPA adsorption when H-MOH300 was used as the adsorbent.

Kinetic Models	Estimated parameters	Experimental data H-MOH300
Pseudo-first-order	q_{eq} (mg g ⁻¹)	7.8 ± 0.3
	k_1 (min ⁻¹)	0.031 ± 0.005
	R^2	0.9909
	χ^2	61.463
Pseudo-second-order	q_{eq} (mg g ⁻¹)	8.6 ± 0.3
	k_2 (g mg ⁻¹ min ⁻¹)	0.005 ± 0.001
	R^2	0.9924
	χ^2	51.218
Intraparticle diffusion model	K_{dif} (mg g ⁻¹ min ^{-0.5})	0.11 ± 0.04
	C (mg g ⁻¹)	4.5 ± 0.9
	R^2	0.4623
	χ^2	2.939
Elovich model	α (mg g ⁻¹ min ⁻¹)	207 ± 232
	β (mg g ⁻¹)	1.5 ± 0.2
	R^2	0.9816
	χ^2	0.101

Figure captions

Figure 1. N₂ physisorption isotherm for H-MOH300.

Figure 2. Particle size distribution of H-MOH300 (cumulative curve and histogram).

Figure 3. Scanning electron microscopy image of H-MOH300.

Figure 4. X-ray diffractogram of H-MOH300.

Figure 5. FTIR spectra of H-MOH300 before and after BPA adsorption.

Figure 6. Point of zero charge (pH_{PZC}) of H-MOH300.

Figure 7. Effect of the pH on the BPA adsorption of H-MOH300 ($C_0 = 20 \text{ mg L}^{-1}$, 22°C, $V = 50 \text{ mL}$, H-MOH300 dosage = 2.0 g L^{-1} , 1440 min, 100 rpm).

Figure 8. H-MOH300 dosage effect on BPA adsorption ($C_0 = 20 \text{ mg L}^{-1}$, 22°C, $V = 50 \text{ mL}$, pH = 6.0, 1440 min, 100 rpm).

Figure 9. Adsorption isotherms for BPA adsorption using H-MOH300 as an adsorbent at different temperatures ($V = 50 \text{ mL}$, H-MOH300 dosage = 2.0 g L^{-1} , pH = 6.0, 960 min, 100 rpm).

Figure 10. Kinetics of BPA adsorption using H-MOH300 as an adsorbent ($C_0 = 20 \text{ mg L}^{-1}$, 22°C, $V = 50 \text{ mL}$, H-MOH300 dosage = 2.0 g L^{-1} , pH = 6.0, 100 rpm).

Figure 11. Proposed mechanism of BPA adsorption onto H-MOH300.

Figure 12. Regeneration of H-MOH300 for BPA adsorption from water during five cycles of adsorption–desorption ($C_0 = 120 \text{ mg L}^{-1}$, 22°C, $V = 250 \text{ mL}$, H-MOH300 dosage = 2.0 g L^{-1} , pH = 6.0, 960 min, 100 rpm).

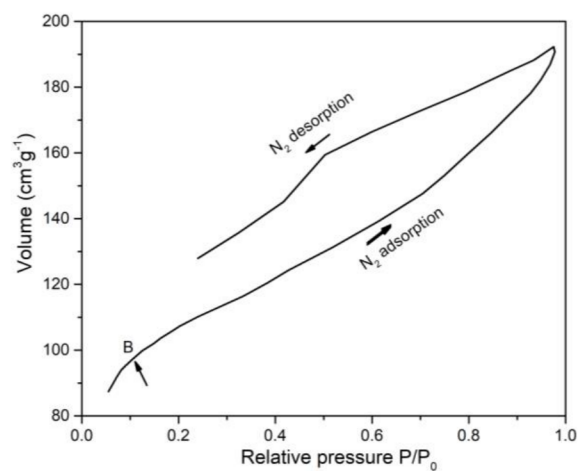
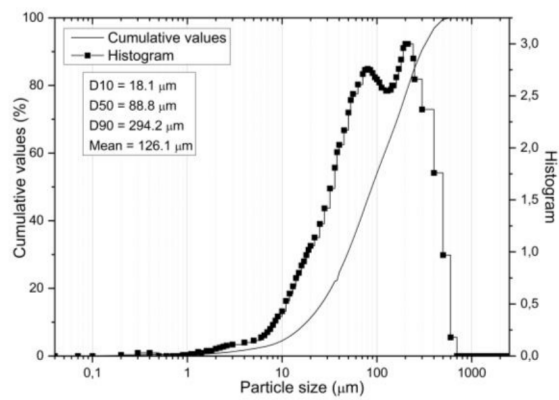
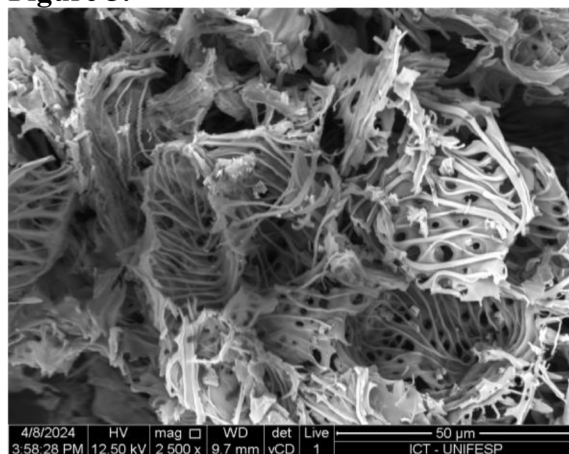
Figure 1.**Figure 2.****Figure 3.**

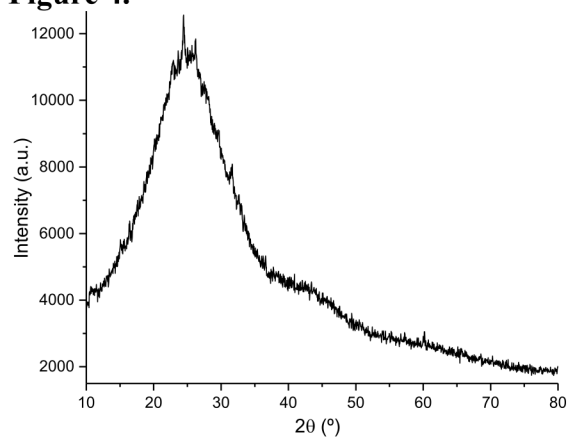
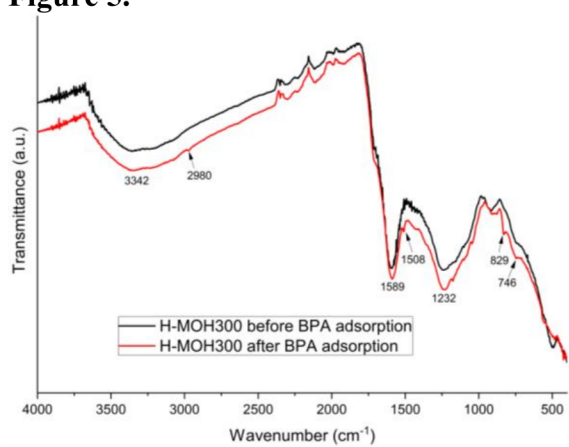
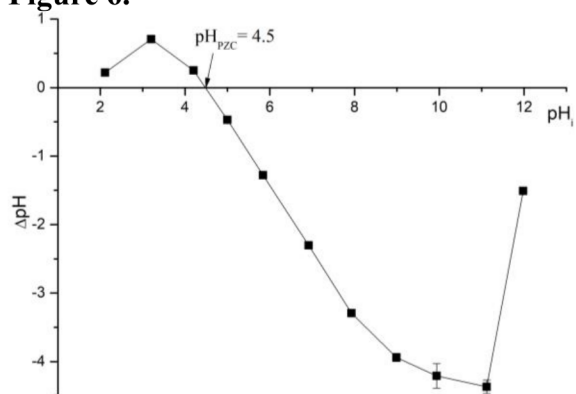
Figure 4.**Figure 5.****Figure 6.**

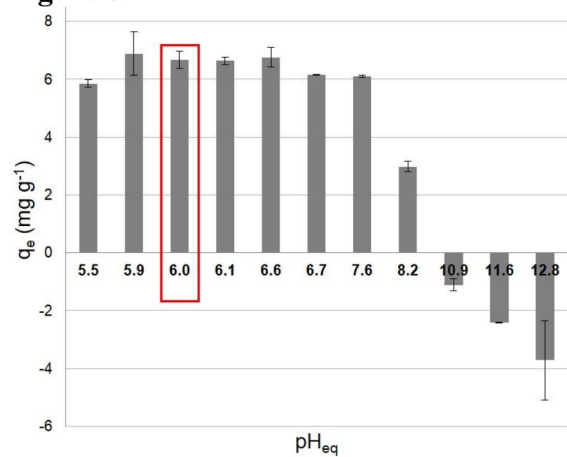
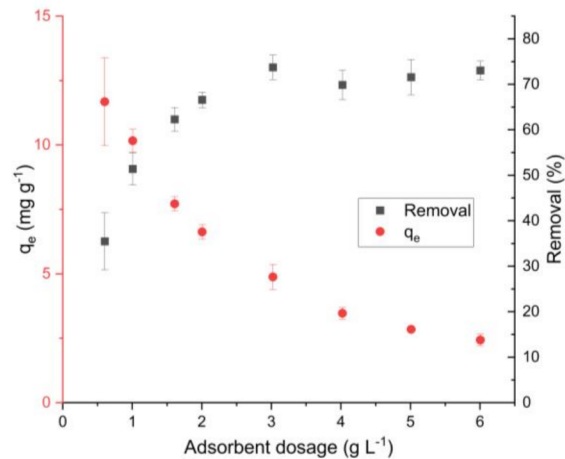
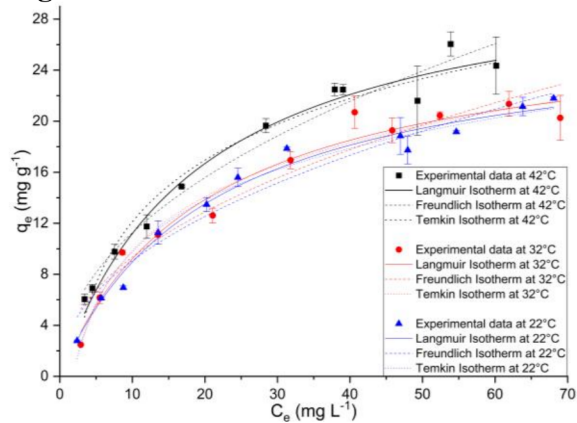
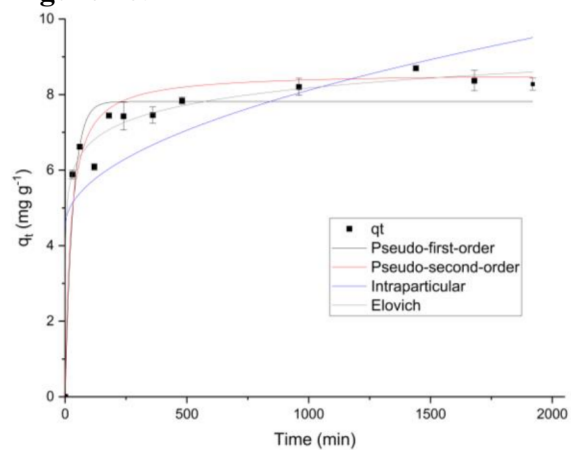
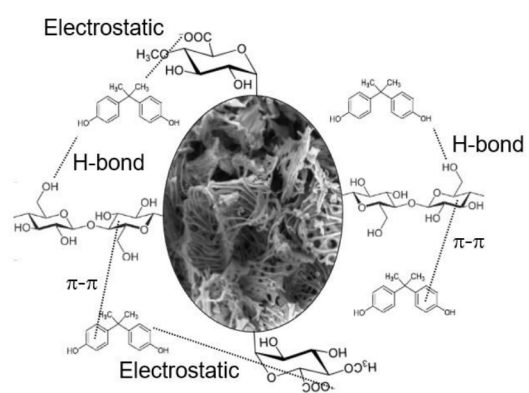
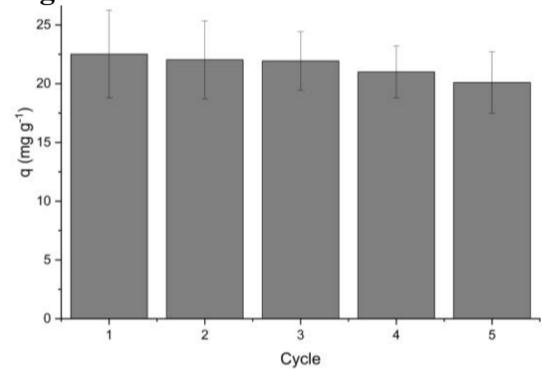
Figure 7.**Figure 8.****Figure 9.**

Figure 10.**Figure 11.****Figure 12.**

4.2 Material Suplementar do artigo sobre o adsorvente desenvolvido

Supplemental material

Bisphenol A quantification method

Figure S1 shows the results of the initial scan carried out with a UV–Vis spectrophotometer (Genesys 50; Thermo Fisher Scientific) with a BPA solution with a 100 mg L⁻¹ concentration.

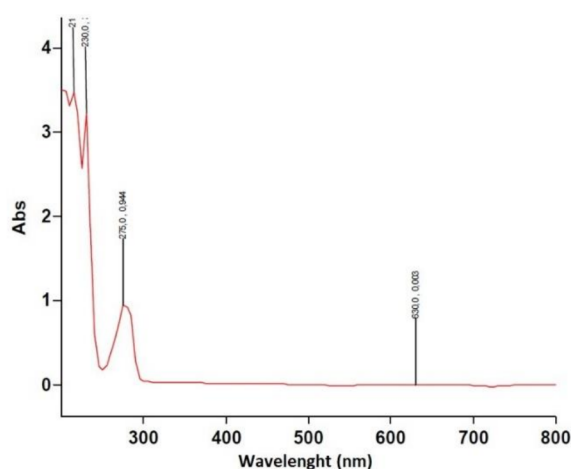


Figure S1. The wavelengths were scanned from 200 to 800 nm, and BPA solution with a 100 mg L⁻¹ concentration was used.

The literature shows that BPA can be quantified at wavelengths between 270 and 290 nm [1–3]. As the scan showed maximum absorbance at 275 nm, a specific analysis was performed between wavelengths of 275 and 280 nm to evaluate the best response (Table S1).

Table S1. Absorbance results of the 100 mg L⁻¹ BPA solution at wavelengths from 275 to 280 nm.

Wavelength (nm)	Absorbance (ABS)
275,0	0,8953
276,0	0,9419
277,0	0,9414
278,0	0,9264
279,0	0,9219
280,0	0,8876

The analytical curve was constructed at 276 nm, as the maximum absorbance obtained in the second test occurred at this wavelength. The analytical range was between 1 mg L⁻¹ and 120 mg L⁻¹ because the water solubility of BPA is 120 mg L⁻¹ at 25°C [4]. Figure S2 shows the first analytical curve developed.

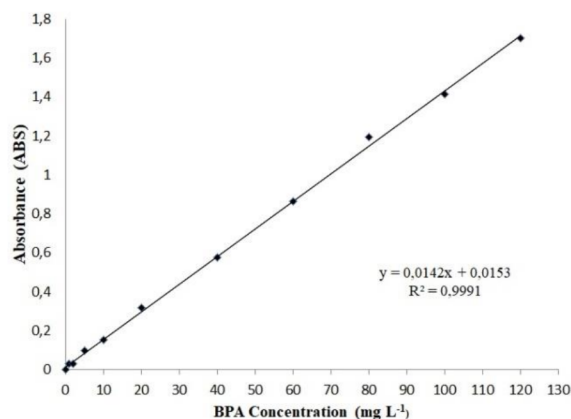


Figure S2. Analytical curve of BPA in water at 276 nm, with a concentration ranging from 1 to 120 mg L⁻¹.

Although the analytical curve showed good linearity, the standard deviations at lower concentrations were high, which increased the error and limit of quantification, compromising quantification in the adsorption tests. Some studies have used of ethanol [5] and methanol [6] to improve the sensitivity of the BPA analytical curve, reducing the deviation between analyses. However, owing to the wide range of dilutions used in the literature, different dilutions of ethanol and methanol were defined for the tests (10%, 25%, 50%, and 75%). Tables S2 and S3 show that the standard deviation percentages decrease throughout the entire concentration range when solvents are added, with the reduction at the lowest concentration being representative.

Table S2. Absorbance results at 276 nm of BPA solutions in water and ethanol.

BPA concentration (mg L ⁻¹)	Water ABS (%DSR)	Ethanol 10% ABS (%DSR)	Ethanol 25% ABS (%DSR)	Ethanol 50% ABS (%DSR)	Ethanol 75% ABS (%DSR)
1,0	0,0289 (17,60)	0,0133 (0,46730)	0,0126 (0,45943)	0,0082 (1,8553)	0,0041 (3,6956)
60,0	0,8642 (0,0364)	0,7658 (0,0345)	0,6787 (0,05175)	0,4946 (0,0)	0,2524 (0,02288)
120,0	1,6999 (0,0748)	1,5400 (0,05522)	1,3657 (0,09575)	1,0003 (0,16088)	0,5083 (0,02272)

Table S3. Absorbance results at 276 nm of BPA solutions in water and methanol.

BPA	Water	Methanol	Methanol	Methanol	Methanol
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concentrati on (mg L⁻¹)	ABS (%DS R)	10% ABS (%DSR)	25% ABS (%DSR)	50% ABS (%DSR)	75% ABS (%DSR)
1,0	0,0289 (17,60)	0,0214 (0, 43519)	0,0133 (0,75188)	0,0067 (0,86602)	0,0032 (3,57124)
60,0	0,8642 (0,0364)	0,7703 (0,00750)	0,6812 (0,11955)	0,8495 (0,02043)	0,2627 (0,28757)
120,0	1,6999 (0,0748)	1,5520 (0,02071)	1,3721 (0,05785)	1,0001 (0,01000)	0,5239 (0,03974)

The new analytical curve (Figure S3) was constructed using BPA solutions in 10% dilution of methanol due to the smaller deviations shown in the tests and because it presents higher absorbance at a concentration of 1 mg L⁻¹ of BPA, improving reproducibility in the low concentration range.

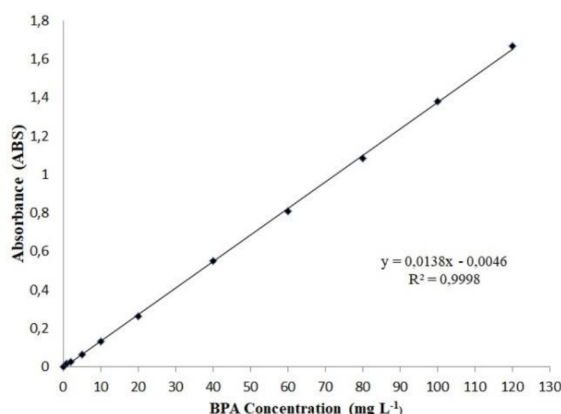


Figure S3. Analytical curve of BPA in methanol 10% at 276 nm, concentration range 1 to 120 mg L⁻¹

From the analytical curve constructed for BPA at the predefined dilution and wavelength, the parameters of linearity, sensitivity, limit of detection (LD), and limit of quantification (LQ) were evaluated [7].

Linearity

The analytical curve was performed in triplicate to evaluate linearity and sensitivity. The correlation coefficient obtained for the curve was 0.9998, which was considered adequate linearity, as the acceptable limit adopted was 0.999 [8].

Limits of Detection and Quantification

The detection limit (LD) is the lowest concentration of the analyte that produces a detectable response above the equipment noise. It is based on the baseline signal-to-noise ratio. This relationship is determined by comparing signals from samples with a known

low concentration to those from samples with no analyte (blank). The acceptable limit for LD is three times the standard deviation obtained in at least ten tests [8].

The Limit of Quantification (LQ) is the lowest concentration of analyte measured with an acceptable level of uncertainty, accuracy, and precision. The permissible limit adopted for LQ is ten times the standard deviation obtained in at least ten tests [8].

Tests were carried out on ten samples with a concentration of 1 mg L⁻¹ of BPA on alternate days to determine the LD and LQ of the spectrophotometric method. The calculations used followed the equations below for the mean (equation 1), the deviation (equation 2), the LD (equation 3), and the LQ (equation 4):

$$X_{msd} = \frac{\sum x_i}{n} \quad (1)$$

$$S = \frac{\sqrt{\sum (x_i - X_{msd})^2}}{n+1} \quad (2)$$

$$LD = 0 + 3S \quad (3)$$

$$LQ = 0 + 10S \quad (4)$$

Table S4 presents the results obtained.

Table S4. LD and LQ calculation data for BPA determination by spectrophotometry

BPA concentration (mg L⁻¹)	 Xi-X_{med} 	X_{med}	S	LD (mg L⁻¹)
1,10	0,010			
1,10	0,010			
1,10	0,010			0,263
1,20	0,090			
1,00	0,110	1,110	0,08756	LQ (mg L⁻¹)
1,20	0,090			
1,20	0,090			
1,00	0,110			
1,20	0,090			0,876
1,00	0,110			

The data set was evaluated for accuracy using the coefficient of variation criteria between results, set as $\leq 15\%$. The coefficient of variation had a value of 7.88%, considered acceptable.

The precision of the data set was also evaluated using the % recovery criteria, that is, comparing the results obtained with the theoretical concentration of 1 mg L⁻¹. The result was 111%, which is considered acceptable as the acceptability criteria are 80% up to 120%.

Although the calculated LQ value was 0.876 mg L⁻¹ of BPA, 1 mg L⁻¹ will be maintained as an expression limit, as this concentration is included in the analytical curve, allowing evaluation of the assay reproducibility over time.

The analytical method for determining BPA by spectrophotometry in the UV range has shown good repeatability and reproducibility throughout the tests.

Adsorption tests equations

Equation of adsorption capacity q (mg g⁻¹):

$$q = \frac{(C_0 - C_e) V}{m} \quad (5)$$

where C_0 and C_e are the initial and equilibrium concentrations of BPA, respectively (mg L⁻¹), V is the volume of BPA solution (L), and m is the adsorbent mass (g).

Pseudo-first order (PFO) equation:

$$q_t = q_e [1 - e^{-k_1 t}] \quad (6)$$

where q_t and q_e are the adsorption capacities at time t and at equilibrium (mg g^{-1}), t is the contact time (min), and k_1 is the pseudo-first-order rate constant (min^{-1}).

Pseudo-second order (PSO) equation:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (7)$$

where q_t and q_e are the adsorption capacities at time t and at equilibrium (mg g^{-1}), t is the contact time (min), and k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

Intraparticle diffusion equation:

$$q_t = K_{dif} \sqrt{t} + C \quad (8)$$

where intraparticle diffusion rate constant is represented by K_{dif} ($\text{mg g}^{-1} \text{min}^{1/2}$), while q_t stands for the adsorption capacity at time t (mg g^{-1}). The variable t represents the adsorption time in minutes and C is the constant related to the thickness of the boundary layer (mg g^{-1}).

Elovich equation:

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \quad (9)$$

where q_t is the adsorption capacity at time t (min), α is the initial rate constant ($\text{mg g}^{-1} \text{mg}^{-1}$), and β is the desorption constant during experiment (mg g^{-1}).

Langmuir isotherm equation:

$$q_e = \frac{q_{max} k_L C_e}{1 + k_L C_e} \quad (10)$$

where k_L is the isothermal constant of Langmuir (L mg^{-1}) and q_{max} is the maximum adsorption capacity (mg g^{-1}).

Freundlich isotherm equation:

$$q_e = K_F C_e^{1/n} \quad (11)$$

where K_F is Freundlich's isothermal constant (mg L^{-1}) (L g^{-1}) $^{1/n}$ and $1/n$ is the Freundlich intensity parameter.

Temkin isotherm equation:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (12)$$

where b_T is the Temkin constant related to adsorption heat (J mol^{-1}), K_T is the isothermal equilibrium constant associated with the maximum binding energy (L mg^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature of the solution (K).

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5 CONCLUSÕES E RECOMENDAÇÕES

5.1 Principal

Esta tese apresentou uma abordagem abrangente para entender e mitigar a contaminação por bisfenol A (BPA) em corpos d'água, com foco em duas frentes: a avaliação da contaminação no rio Paraíba do Sul e o desenvolvimento de um adsorvente ecológico utilizando cascas de sementes de *Moringa oleifera*.

Os resultados evidenciam que o BPA e outros compostos que são desreguladores endócrinos é uma preocupação significativa para a qualidade da água, exacerbada por uma infraestrutura de tratamento de esgoto inadequada, como é o caso do trecho paulista do rio Paraíba do Sul.

Essa pesquisa também demonstrou a viabilidade do uso de resíduos agrícolas, especificamente a biomassa de casca da semente de *Moringa oleifera* ativada quimicamente com ácido fosfórico e termicamente a 300°C, como um adsorvente eficaz para a remoção de BPA. Este adsorvente mostrou boa capacidade de adsorção e potencial para reutilização, oferecendo uma solução sustentável e de baixo custo para a remediação de águas contaminadas.

5.2 Recomendações

Com base nos achados desta tese, são feitas as seguintes recomendações:

1. **Melhoria da Infraestrutura de Tratamento de Efluentes:** É essencial investir no aumento da cobertura de tratamento de efluentes, diminuindo a carga orgânica remanescente que chega aos corpos hídricos que são usados como fonte de água para abastecimento público. Isso inclui a modernização de estações de tratamento de esgoto existentes e a construção de novas instalações.
2. **Monitoramento Contínuo:** Implementar programas de monitoramento contínuo da qualidade da água para detectar a presença de BPA e outros poluentes emergentes. Este monitoramento deve ser realizado em múltiplos pontos dos corpos d'água e incluir análises regulares para avaliar os níveis de contaminação e sua relação com outros parâmetros de qualidade da água.

3. **Incentivo à Pesquisa e Desenvolvimento:** Apoiar pesquisas que explorem novas tecnologias e materiais para a remoção de contaminantes emergentes. O desenvolvimento de adsorventes de baixo custo, como a casca de sementes de *Moringa oleifera*, deve ser incentivado por meio de financiamento e colaborações interdisciplinares.
4. **Valorização de Resíduos Agrícolas:** Promover estudos para o uso de resíduos agrícolas, como a casca de sementes de *Moringa oleifera*, em aplicações ambientais. Programas de reciclagem e reutilização de resíduos podem não só ajudar na remediação ambiental, mas também fornecer uma fonte adicional de renda para comunidades agrícolas.

As conclusões e recomendações desta tese ressaltam a necessidade de ações coordenadas entre governos, indústria, academia e sociedade para enfrentar os desafios da contaminação por poluentes emergentes. A combinação de monitoramento rigoroso e tecnologias de remediação ecológicas podem contribuir significativamente para a proteção dos recursos hídricos e da saúde pública.

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7 ANEXOS

7.1 Comprovante de submissão do artigo sobre a contaminação com BPA do rio Paraíba do Sul



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Submission Confirmation for A Comprehensive Study on Bisphenol A and Estrogenic Activity in the Paraíba do Sul River, São Paulo, Brazil

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