# PHYTOREMEDIATION, BIOACCESSIBILITY AND ECOTOXICOLOGICAL RISK ASSESSMENT OF ARSENIC

**Aluna:** Elida Cristina Monteiro de Oliveira

**Orientador:** Prof. Dr. Boscolli Barbosa Pereira

**UBERLÂNDIA - MG**
**2022**

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Dissertação apresentada à Universidade Federal de Uberlândia como parte dos requisitos para obtenção do Título de Mestre em Genética e Bioquímica (Área Genética)

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Coordenação do Programa de Pós-Graduação em Genética e Bioquímica

Av. Pará 1720, Bloco 2E, Sala 244 - Bairro Umuarama, Uberlândia-MG, CEP 38400-902

Telefone: +55 (34) 3225-8438 - www.ppggb.ibtec.ufu.br - ppggb@ufu.br

## ATA DE DEFESA - PÓS-GRADUAÇÃO

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Aos dezenove dias do mês de dezembro de dois mil e vinte e dois, às 16:50 horas, reuniu-se via web conferência pela plataforma Cisco Webex, em conformidade com a Portaria nº 36, de 19 de março de 2020 da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES e Resolução de nº 06/2020 do Conselho de Pesquisa e Pós-graduação pela Universidade Federal de Uberlândia, a Banca Examinadora, designada pelo Colegiado do Programa de Pós-graduação em Genética e Bioquímica, assim composta: Professores Doutores: Boscolli Barbosa Pereira (Orientador), Edimar Olegário de Campos Júnior e Luis Paulo Pires. A participação dos dois últimos se deu por epístola. Iniciando os trabalhos o (a) presidente Dr (a). Boscolli Barbosa Pereira apresentou a Comissão Examinadora e o candidato(a), agradeceu a presença dos participantes, e concedeu ao Discente a palavra para a exposição do seu trabalho. A duração da apresentação do Discente e o tempo de arguição e resposta foram conforme as normas do Programa. A seguir o senhor (a) presidente procedeu a leitura das epístolas enviadas pelos membros da banca. Em seguida os membros presentes, passaram a arguir o(a) candidato(a). Ultimada a leitura das epístolas e a arguição, que se desenvolveu dentro dos termos regimentais, a Banca, em sessão secreta, atribuiu o resultado final, considerando o(a) candidato(a):

( A ) PROVADO.

Esta defesa de Dissertação de Mestrado é parte dos requisitos necessários à obtenção do título de Mestre. O competente diploma será expedido após cumprimento dos demais requisitos, conforme as normas do Programa, a legislação pertinente e a regulamentação interna da UFU. Nada mais havendo a

tratar foram encerrados os trabalhos. Foi lavrada a presente ata que após lida e achada conforme foi assinada pela Banca Examinadora.

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# PHYTOREMEDIATION, BIOACCESSIBILITY AND ECOTOXICOLOGICAL RISK ASSESSMENT OF ARSENIC

**ALUNA:** Elida Cristina Monteiro de Oliveira

## COMISSÃO EXAMINADORA

**Presidente**: Prof. Dr. Boscolli Barbosa Pereira (Orientador)

**Examinadores:**

Edimar Olegário de Campos Júnior

Luis Paulo Pires

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PROF. DR. BOSCOLLI BARBOSA PEREIRA

Dedico este trabalho à Deus, à minha filha Amanda, que sempre me apoiou e incentivou e aos meus irmãos Taynara e Matheus, por sempre estarem a meu lado.

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# SUMMARY

## APRESENTAÇÃO

A exploração dos recursos minerais cresceu significativamente nas últimas décadas, resultando no comprometimento da qualidade ambiental. Há significativo consenso na comunidade científica de que a mineração constitui atividade predatória ao ambiente, especialmente no que se refere à qualidade das águas no entorno e à jusante da área de exploração, que pode ser prejudicada em razão da turbidez provocada pelos sedimentos finos em suspensão, assim como pela poluição causada por substâncias lixiviadas, carreadas ou contidas nos efluentes, tais como óleos, graxa e metais pesados - estes podem também atingir as águas subterrâneas.

Entre os impactos negativos oriundos da mineração pode-se citar a contaminação por arsênio (As). Em várias partes do mundo e em algumas localidades no Brasil, têm sido mensurados elevados teores de arsênio em águas superficiais e subterrâneas, solos e em rejeitos presentes em áreas mineradoras. Em suma, a disponibilidade dos metais pesados depende da presença destes elementos na água ou sedimento e de sua tendência em formar compostos precipitados insolúveis e coprecipitados com outros minerais para formar complexos com matéria orgânica e adsorver outros minerais. Nesse contexto, a avaliação da contaminação das águas em áreas de mineração é fundamental para a avaliação, monitoramento, prevenção e mitigação dos impactos ambientais.

Nesta conjuntura, o primeiro capítulo desta dissertação busca apresentar e discutir alguns aspectos relevantes relacionados à contaminação dos ambientes aquáticos por As, avaliando impactos e soluções biotecnológicas sustentáveis, segundo a perspectiva do campo da Saúde Ambiental. O segundo capítulo apresenta os resultados de um estudo realizado *in situ* utilizando a macrófita *Hydrocotyle ranunculoides* L. para avaliar tanto o potencial uso da espécie na avaliação do risco ecotoxicológico, bem como sua aplicação em ações de fitorremediação de metais pesados.

# CHAPTER 1. ARSENIC EXPOSURE FROM GROUNDWATER: ENVIRONMENTAL CONTAMINATION, HUMAN HEALTH EFFECTS, AND SUSTAINABLE SOLUTIONS

**ABSTRACT**

Arsenic (As) occurs naturally in geologic conditions, but groundwater contamination might also be found due to the consequences of mining, agricultural and industrial processes. Human exposure to As after drinking contaminated water is commonly associated with acute toxicity outcomes and chronic effects ranging from skin lesions to cancer. Integrated actions from environmental and health authorities are needed to reduce exposure, monitoring outcomes, and promotion of actions to offer sustainable As-safe water alternatives. Considering recent research trends, the present review summarizes and discusses current issues associated with the process and effects of contamination and decontamination in an environmental health perspective. Recent findings reinforce the harmful effects of the consumption of As-contaminated water and broaden the scope of related diseases including intestinal maladies, type 2 diabetes, cancers of bladder, kidneys, lung, and liver. Among the main strategies to diminish or remove As from water, the following are highlighted (1) ion exchange system and membrane filtration (micro, ultra, and nanofiltration) as physicochemical treatment systems; (2) use of cyanobacteria and algae in bioremediation programs and (3) application of nanotechnology for water treatment.

**Keywords:** Toxicology; methylation; cancer; arsenicosis; drinking water; nanotechnology

# 1 INTRODUCTION

As the number of people exposed to arsenic (As) contamination in the world grows, the need for investigations of the main routes of this contamination, health impacts, and mitigation possibilities has increased. According to the US Environmental Protection Agency standard for public water systems (USEpa 2017) and the World Health Organization drinking water standard (WHO 2017), contamination of drinking water containing As at concentrations above 10 µg/L (recommended limit of arsenic in drinking-water) affects at least 140 million individuals in 50 countries and is considered one of the major challenges faced by public health. Based on this fact, investigations conducted in different countries and continents demonstrated situations of enhanced adverse health risk attributed to chronic exposure to water contaminated by As, especially when consumed directly from artesian wells (Chiu and Yang 2005; Greco et al. 2019; Rogers et al. 2019).

Interestingly, although As occurs naturally in geologic conditions, groundwater contamination might also be present due to consequences of anthropogenic actions from (1) mining activities, (2) use of As-based pesticides and herbicides in agriculture, (3) industrial processes, and (4) irrigation (Sarkar and Paul 2016; Zheng 2017). Groundwater contamination via irrigation is a problem because the process of collecting the water, with pumping large volumes of water at a high rate, changes the water flow patterns and thereby As concentrations enhance groundwater contamination (Zhang et al. 2019).

The inorganic form of As, naturally present in the groundwater, is predominantly associated with acute toxicity outcomes (Ahmad, Khan, and Haque 2018; Baker, Cassano, and Murray 2018). Arsenic is tasteless, colorless, and does not smell, and thus difficult to perceive acute effects since high doses are usually necessary for the manifestation of acute unintentional toxicity. Based upon the lack of taste, color, and smell exposure to As tends to become chronic after drinking contaminated water tends with effects ranging from skin lesions to cancer (Hong et al. 2017; Palma-Lara et al. 2020; Tsuji et al. 2019).

While As contamination of drinking water is a serious concern worldwide, integrated management still requires facing different challenges, including political, social, economic, and technical determinants. In this context, research and health

promotion actions are critical to (1) offer sustainable As-safe water alternatives; (2) provide a realistic testing of the metalloid in drinking water; and (3) monitor the effects of metal-induced toxicity, thereby promoting effective public health surveillance to reduce exposure and monitoring outcomes.

Thus, considering the research gap between groundwater As contamination issues and the urgency to deliver sustainable biotechnology solutions to their management, this review aimed to summarize and discuss relevant aspects related to the topics contamination, effects, and decontamination in an environmental health perspective.

## 2 GLOBAL CONTAMINATION OF GROUNDWATER BY As

Contamination of groundwater by As continues to be a major concern worldwide. Populations exposed to high concentrations of As are susceptible to harmful health effects due to the presence of this environmental contaminant in drinking water. Thus, it is imperative to define guidelines that indicate a concentration considered safe for daily consumption of drinking water (Bacquart et al. 2015). Based upon toxicological evidence, the World Health Organization (WHO 2017) established the maximum allowable concentration of As equivalent to the limit of 10 µg/L. However, studies conducted in aquifers from various parts of the world have reported concentrations of As above this standard, causing serious public health concerns (Ali et al. 2019; Rahman and Rahaman 2018; Rahman et al. 2018). Table 1 presents the concentrations of As detected in groundwater in different countries which are distributed in most continents.

**Table 1.** Concentrations of as found in groundwater in different countries

| Continent | Country | Local (urban/rural) | Type (public/private) | Concentracion of As (µg/L) | Reference |
|---|---|---|---|---|---|
| American | Canada | Rural | Private | ≤ 326 | Bondu et al. 2017 |
| | Nicaragua | Rural | Uninformed | ≤ 1320 | Quezada, Espinoza, and Bundschuh 2020 |
| | Argentina | Rural | Public | ≤ 535 | Alcaine et al. 2020 |
| | Peru | Urban and rural | Public | ≤ 715 | Meyer et al. 2017 |
| African | Burkina Fasso | Rural | Uninformed | ≤ 421 | Bretzler et al. 2017 |
| European | Greece | Urban and rural | Uninformed | ≤ 25 | Dokou, Kourgialas, and Karatzas 2015 |
| | Italy | Uninformed | Uninformed | ≤ 431 | Carraro et al. 2015 |
| | Ireland | Uninformed | Public and Private | ≤ 471 | McGrory et al. 2017 |
| Asian | China | Uninformed | Uninformed | ≤ 377 | Wang et al. 2018 |
| | China/Taiwan | Uninformed | Uninformed | ≤ 544 | Liang et al. 2017 |
| | India/Majuli | Rural | Uninformed | ≤ 386 | Goswami et al. 2020 |
| | India/Bhojpur | Rural | Uninformed | ≤ 168 | Maity, Biswas, and Sarkar 2020 |
| | India/KMC | Urban | Uninformed | ≤ 800 | Chakraborti et al. 2017 |
| | Myanmar | Urban and rural | Private | ≤ 134 | Bacquart et al. 2015 |
| | Bangladesh/Kushtia | Rural | Uninformed | ≤ 590 | Huq et al. 2019 |
| | Bangladesh | Uninformed | Uninformed | ≤ 263 | Khan and Bakar 2020 |
| | Pakistan | Urban and rural | Uninformed | ≤ 132 | Shahid et al. 2018 |

Smedley and Kinniburgh (2002) reported high levels of As in various countries, including Argentina, Bangladesh, China, and Pakistan, among others. These findings corroborate observations that indicate high concentrations of the metalloid in groundwater in these and other countries suggesting that life-threatening metalassociated conditions remain in these regions even after more than a decade (Alcaine et al. 2020; Bacquart et al. 2015; Khan and Bakar 2020; Liang et al. 2017; McGrory et al. 2017; Shahid et al. 2018).

In Argentina, As concentrations ranged from 5.9 to 535.1 µg/L with an average of 114 µg/L in groundwater samples from the studied area (Alcaine et al. 2020). Accordingly, the majority of the wells exceeded the WHO guideline allowed for As. The maximal concentration found was 535 µg/L surpassing the threshold limit and thus, rendering the water unsuitable for human consumption (Alcaine et al. 2020).

Huq et al. (2019) noted a similar result in samples of Bangladesh, Kushtia district. The concentration of As in drinking water varied from 6.04 to 590.7 µg/L with a mean of 59.73 µg/L also exceeding the WHO guideline more than 50- fold. The standard limit in Bangladesh (50 µg/L) was exceeded 10-fold. Further, in Majuli, India, As concentrations ranged from 5 to 386 µg/L (average 137 µg/L) with samples surpassing the WHO limit. In Myanmar (Bacquart et al. 2015) and Burkina Faso (Bretzler et al. 2017) As concentrations ranged from 1 to 134 µg/L and from 0.02 to 421 µg/L, respectively.

The analysis of the samples in these investigations indicated the presence of other contaminants in addition to As, such as iron (Fe), manganese (Mn), copper (Cu), and fluoride (F), which often exceeded the limit allowed by WHO (Bondu et al. 2017; Carraro et al. 2015; Meyer et al. 2017; Rotiroti et al. 2017; Serrazina et al. 2018).

Previously Podgorski et al. (2017) showed high concentrations of As in water consumed by a large part of the population all around the world. Exposure to As-contaminated aquifers was reported to threaten 150 million people throughout the world (Podgorski et al. 2017). In fact, tubular wells are the main source of contaminated water especially in rural regions (Bretzler et al. 2017; Huq et al. 2019; Khan and Bakar 2020; Quezada, Espinoza, and Bundschuh 2020).

Although As mobilization occurs naturally from sediment to groundwater through redox processes, the act of digging wells and using chlorine for sanitation also boosts the release of As and other metals into water, thus disturbing the aquifer and inducing a geochemical disequilibrium. Erickson et al. (2019) found in Florida groundwater disturbances after installation of public-supply wells and domestic wells. Further, over time As concentrations may increase as a result of pumping. This process promotes changes in redox conditions, thus affecting As mobility and mixing different waters toward distinct directions to the well (Erickson et al. 2019).

Although well-drilling may disturb aquifer geochemical equilibrium and increase As levels, there are also other sources of contamination. The accumulation of metalloid and its mobilization might occur via natural processes such as volcanic activities, weathering of volcanic rocks, hydrothermal, geothermal, and microbial activities, but different anthropogenic activities, as mentioned early, including mining and use of As-based pesticides and herbicides also contribute to the availability of metalloid in soil and sediments (Flora 2015; Sharma et al. 2016). Arsenic commonly co-occurs with other contaminants such as Cd, Cu, Fe, Pb, Ni, and Zn especially from gold mining operations (Lopez-Barrera and Barragan-Gonzalez 2016; Serrazina et al. 2018). Hence, global mining activities have resulted in the release of As into groundwater for over a century (Teixeira et al. 2020).

Highest concentrations of As in groundwater are found due to mineral water interactions and favorable conditions. In groundwater, As mobilization and accumulation are dependent on climatic and physicochemical factors of soil–water interactions, such as pH, redox conditions, and chemical (mineralogical) composition of soil and sediments (Smedley and Kinniburgh 2002). Therefore, assessing and evaluating different exposure sources, environmental use and conditions of groundwater in each region around the world might provide the selection of effective technological health solutions that are site-specific. In this context, Table 4 shows different examples of contamination sources.

**3 IMPACTS OF EXPOSURE TO As ON HEALTH**

The consumption of groundwater contaminated with As is the main source of exposure to this contaminant for humans, but other important sources must be considered, such dermal, as well as other routes of exposure including dermal (Rahman et al. 2018; Zhang et al. 2019) and by intake of rice and vegetables (Nancano, Freitas, and Barbosa 2014).

In the human body, arsenite binds to thiol groups found in proteins of different tissues, including lung, spleen, liver, kidneys, and gastrointestinal mucosa, and this metalloid may be harmful even at low concentrations. Further, arsenite inhibits pyruvate dehydrogenase (PDH) complex through interaction with the active form of lipoic acid, lipoamide, thereby interfering with cellular energy metabolism (Costa 2019). The toxicity of arsenate is triggered by the inactivation of several enzymes, especially those related to DNA synthesis and repair, and in the production of energy for cells (Souza et al. 2019). Recently, Chang and Singh (2019) investigated As-induced carcinogenicity in renal epithelial cells and found no significant effects on cell growth rate following acute72 hr treatment.

Chronic exposure to As has been associated with harmful effects on human health. In fact, the presence of contaminating elements was noted to enhance adverse health risks in humans. Table 2 displays the damage initiated to various organs resulting from chronic exposure to As according to different studies (Ahmed et al. 2017; Chakraborti et al. 2017; Edmunds, Ahmed, and Whitehead 2015; Goswami et al. 2020; Harmon et al. 2018; Powers et al. 2018; Roh et al. 2018).

**Table 2.** Effects observed after chronic exposure to As

| Target organs | Observed effects | References |
|---|---|---|
| Integumentary System (Skin) | Skin lesions; arsenicosis (symptoms: keratosis, melanosis, keratosis, leukomelanosis); Bowen's disease; squamous cell carcinoma | Edmunds, Ahmed, and Whitehead 2015; Chakraborti et al. 2016; Kuo, Lo, and Guo 2017; Chakraborti et al. 2017 |
| Respiratory system (Lung, larynx) | Lung cancer, larynx cancer, alteration of the airways, impaired lung function, cough, shortness of breath | Roh et al. 2018; Ahmed et al. 2017; Chakraborti et al. 2017; Powers et al. 2018; Smith et al. 2018 |
| Cardiovascular system (Blood vessels, heart) | Peripheral vascular disease, hypertension | Edmunds, Ahmed, and Whitehead 2015 |
| Urinary system (Kidney, bladder) | Kidney, bladder cancer | Antoni et al. 2017; Narayan et al. 2018; Smith et al. 2018; Goswami et al. 2020 |
| Nervous system (Nerves, brain) | Neuropathy (symptoms: distal paresthesia, pain in the limbs, hyperpathy, signs of hypoesthesia in distal limbs), headache | Chakraborti et al. 2017 |
| Auditory system (Ear) | Dizziness, vertigo | Chakraborti et al. 2017 |
| Endocrine system (Pancreas) | Diabetes | Edmunds, Ahmed, and Whitehead 2015 |
| Reproductive system (Prostate, uterus) | Increased incidence of prostate cancer, spontaneous abortions | Roh et al. 2017; Chakraborti et al. 2017 |

Arsenic is absorbed primarily through inhalation and oral consumption, as well as through contact via dermal exposure or mucous membranes. The toxicokinetics of the pro-oxidant element depends upon the type and duration of exposure, chemical characteristics, and physicochemical aspects. Direct oral exposure (ingestion of contaminated water) and indirect exposure (consumption of food grown with contaminated water) are the main forms of exposure among all absorption routes responsible for numerous metalloid-related pathologies worldwide (Chakraborti et al. 2017; Rahman et al. 2018).

Regarding chronic exposure, non-cancerous skin lesions are characterized as the most prominent feature used in the identification of individuals with arsenicosis-specific symptoms of As poisoning. In view of this, investigators consider these skin lesions as a clinical marker of susceptibility to the contaminant (Chakraborti et al. 2017; Edmunds, Ahmed, and Whitehead 2015).

Exposure to As is directly proportional to water intake and concentration in water. Interestingly, the average of direct and indirect water consumption by individuals from different countries is highly varied. Chakraborti et al. (2017) found that the harmful dermatological manifestations occur at various concentrations of As in drinking water. Populations exposed to concentrations of 50 µg/L, national guideline of many developing countries, exhibited severe skin lesions (Huq et al. 2019; Rahman and Rahaman 2018; Rahman et al. 2018). However, Yoshida, Yamauchi, and Fan Sun (2004) observed skin lesions at even lower exposure levels in the range of 0.005–0.01 mg/L As in drinking water.

Individuals chronically exposed to As develop non-cancerous (arsenicosis) and cancerous skin lesions, such as basal-cell carcinoma and squamous-cell carcinoma, in addition to Bowen's disease. Systemic toxicity induced by As is associated with the risk of skin cancer and incidence of internal cancers (lung, bladder, liver, and kidney), as well as respiratory and neurological disorders (Mochizuki 2019; Sinha and Prasad 2020; Smeester and Fry 2018). Smith et al. (2018) suggested that lung cancer is the most common determinant for As-related mortality, even after decades of reducing the exposure to the contaminanT.

The findings regarding the cancerous effects initiated by exposure to As are consistent with observations of Roh et al. (2018) and numerous other epidemiological studies reporting the incidence and mortality resulting from the

development of cancer directly associated with As exposure (Ahmed et al. 2017; Antoni et al. 2017; Chakraborti et al. 2017; Chiu et al. 2004; Goswami et al. 2020; Kuo, Lo, and Guo 2017; Narayan et al. 2018).

Chakraborti et al. (2017) reported that inorganic forms of As in chronically exposed women cross the placenta and, therefore, may affect reproductive and developmental processes of the unborn child. Other confounding factors may also contribute to reproductive and developmental disorders, for instance, the period of exposure and concentration at source, the minimum level of metalloid needed to produce a congenital malformation, repeated childbirth, and malnutrition in populations chronically exposed to As. Spontaneous abortions, stillborn, premature births, low weight at birth, and neonatal deaths are more prevalent among chronically-As exposed populations (Chakraborti et al. 2017).

Although As is not considered directly genotoxic (Demanelis et al. 2019), this metalloid induces oxidative stress, inflammation and may produce epigenetic dysregulation. Table 3 shows human ailments initiated by As exposure and associated epigenetic effects. Indeed, when metabolized in the body and throughout the methylation process, As generates reactive oxygen species (ROS), such as superoxide, peroxyl, and hydroxyl groups, and mitochondrial enzyme activities are modified in the transference of electrons from the respiratory chain (Mar Wai et al. 2019). Therefore, due to the potential concern resulting from As exposure to human health, investigators have made strides to improve the understanding of this environmental contaminant.

**Table 3.** Human ailments caused by arsenic exposure and epigenetic effects.

| Epigenetic Consequences | Chemical-cellular interaction | References |
|---|---|---|
| Kidney Cancer | Modulation of proteins related to tumor suppressor genes: BAP1, RELA, TP53, VHL | Polo et al. 2018 |
| Bladder Cancer | Modulation of proteins related to tumor suppressor genes: PABPC1, TNF, KRAS, CCNE 1 | Polo et al. 2018 |
| Malignant transformation in human bronchial epithelial | Inhibition of miRNA-31 expression, overexpression of special AT-rich sequence-binding protein 2 (SABT 2) | Chen et al. 2018 |
| Cancerous and precancerous skin lesions | DNA methylation: Regions of tumor suppressor p16 and DAPK genes | Bjørklund et al. 2018 |
| Toxicity in human urothelial cells | Decreased histone 4 lysine 16 acetyltransferase (H4K16Ac); miRNA dysregulation | Bjørklund et al. 2018; Cardoso, Al-Eryani, and States 2018 |
| Induction of autophagy in hepatic epithelium | Decreased expression of miR-21 target proteins, upregulation of miR-21 levels in a concentration-dependent manner | Cardoso, Al-Eryani, and States 2018 |
| Diabetes | DNA methylation: Inhibition of glucose-stimulated insulin secretion (GSIS) | Khan et al. 2017 |
| Neurological diseases: Parkinson, Alzheimer | Form plaques and enter the substantia nigra (SN), effect on dopaminergic brain function | Costa 2019 |
| Atherosclerosis | Hypermethylation and transcripted depression of ATP-binding cassette transporter A1 (ABCA1) causing plasma HDL-C decrease. Up-regulate oxidation-related: glutathione-S-transferase and thioredoxin reductase | Song et al. 2019 |

**Table 4.** Origins of groundwater and drinking-water contamination by arsenic in different regions

| Region | Zone | Sources | Contamination routes | Physical-chemical mechanisms | References |
|---|---|---|---|---|---|
| Bangladesh | Rural | *Domestic well/Natural sources | Deposition of large volumes of arsenic-containing sediments due to sedimentary basin structure | Leaching/Oxidation processes, Microbial metabolism | Ahmad et al. 2018 |
| Brazil | Urban | Mining activities, industrial pollution, geochemical anomalies | Arsenopyrite-bearing wastes deposition/manganese, gold pelletizing process/ agrochemicals | Leaching/Chemical weathering processes | Teixeira et al. 2020; Souza et al. 2019 |
| United States, China, Vietnam | Rural and urban | Natural sources *Domestic well | Arsenic-bearing sulfide minerals/rocks sediments, Geochemical conditions, Arsenic-enriched geothermal deposits | Leaching/Oxidation processes/ reductive dissolution and desorption/ion concentration, and ion competition; | Podgorski and Berg 2020; Ayotte et al. 2017 |
| Latin American, Central American | Rural and urban | *Domestic well Natural sources | Geothermal reservoirs, and Volcanic Rocks | Leaching/Redox processes, alkali desorption | Morales-Simfors et al. 2020; Rodriguez et al. 2019 |
| India | Rural | *Domestic well Natural sources | Natural deposition of arsenic-rich pyrite | Mobilization: microbial respiration of organic carbon | Chakraborti et al. 2018 |

*Domestic Well (private or homeowner wells)

## 4 STRATEGIES FOR TREATMENT OF ARSENIC

The occurrence of As in groundwater poses enhanced risks to adverse environmental and human health. Arsenic is considered a potential human carcinogen, and consumption of metalloidcontaminated water induces several lifethreatening diseases, including intestinal maladies, type 2 diabetes, cancers of bladder, kidneys, lung, and liver, and ultimately death (Rahman et al. 2020). The following section and Table 5 describe different strategies to either reduce or remove As from water. Importantly, these strategies might be fully exploited in the near future for water treatment.

**Table 5.** Different strategies to reduce or remove arsenic from water

| Removal strategy | Technique | Mechanism | Removal efficiency of As | Advantages | Disadvantage | Reference |
|---|---|---|---|---|---|---|
| Arsenic-removal filters | Point-of-entry | Filtration system installed at main water line to purify all water entering a house | 95% | Use in small systems | Requires filter maintenance Higher cost Formation of biofilm | Yang et al. 2020 |
| | Point-of-use | Filtration system placed at a single tap | 95% | Effective for small systems. POU devices can be coupled with reverse osmosis | Treatment of only one tap Requires filter maintenance | Yang et al. 2020 |
| Physico-chemical technique | Ion exchange | Use of synthetic resin beds | 95% | pH independent. Interference of several factors. | Only efficient for arsenite removal. Replacement of resin. Highly concentrated waste by-product. | Chen et al. 2020 |
| Membrane filtration | Microfiltration/ Ultrafiltration | Low pressure-driven separation of ions | 95% at low concentration 40–65% at high concentration | Ease of operation. Consume low energy. Low cost. | Low efficiency of arsenic removal. Both require other techniques to improve the effectiveness of treatment. | Lohokare et al. 2008; Sarkar and Paul 2016; Wan et al. 2020 |
| | Nanofiltration | High pressure separation of ions | > 95% | High As(V) removal efficiency | Requires extensive corrosion control. Pre-oxidation process is need for removal As(III). | Schmidt et al. 2016 |
| | Reverse osmosis | High pressure separation of ions | 86–99% | High As(V) removal efficiency. Safe to handle. Easy maintenance. | High investment cost Requires extensive corrosion control | Schmidt et al. 2016 |
| Cyanobacteria and algae | *Leptolyngbya boryana* | Intracellular accumulation and tolerance of arsenic | > 95% | Cyanobacterium widely distributed in freshwater ecosystems | Genes involved in arsenic biotransformation are still unknown | Zhu et al. 2020 |
| | *Nostoc sp* | Intracellular uptake of arsenic | 90% | Ubiquitous in freshwater ecosystems. Multiple arsenic biotransformation pathways. Able to survive at high concentrations of arsenic | Bioaccumulation of As in the cyanobacterial biomass could impair its use in waste water treatment | Ferrari et al. 2013; Xue et al. 2017 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | *Nostoc muscorum* | Intracellular accumulation of As(III) and As(V) | 90% | Nutrient supplementation can be used to enhance the accumulation of arsenic | Lack of studies using the strain. Bioaccumulation of As in the biomass; risk of arsenic to enter in the food chain. | Cepoi et al. 2016; Patel, Tiwari, and Prasad 2018 |
| | *Microcystis aeruginosa* | Removal and bioremediation of arsenic from water | 95% | High uptake of As(V). Accumulation, methylation or transformation pathways of arsenic to less toxic species. | Further studies are required regarding the long-term effects of As on the species | Wang, Luo, and Yan 2013; Wang et al. 2015 |
| Nanoparticles | ZIF-8 nanoparticles | Adsorption of As(III) and As(V) | > 97% | High stability in water. High thermal and mechanical stability. Chemical robustness | Lack of mechanistic understanding on ultrastructure morphology. Cost-effective synthesis route | Jian et al. 2015; Haldar, Duarah, and Purkait 2020 |
| | Copper oxide nanoparticles | Adsorption of aqueous arsenic species | 88.4–97.8% | High As(III) removal efficiency | High cost of materials | Kumar, Ranjan, and Quaff 2020 |

## 4.1 PHYSICOCHEMICAL TREATMENT SYSTEMS

Deteriorating water quality and increasing awareness regarding carcinogens as well as other toxic compounds are among the factors driving the surge to seek alternatives to reduce As concentrations. In natural waters, As occurs predominantly in the oxidation states +III (arsenite) and +V (arsenate). It is noteworthy that the effective removal of the trivalent form has attracted increasing attention due to its higher toxicity and neutral charge in the groundwater, which hamper removal processes. Indeed, arsenite is approximately 60-fold more harmful than arsenate and is also more difficult to remove from water (Singh et al. 2015). In this context, various household water treatment technologies were also developed to initially oxidize As(III) to As(V) prior to adsorption and removal (Zhang et al. 2020).

### 4.1.1 Point-of-entry and point-of-use systems

The major types of physicochemical As treat  ment systems include point-of-entry (POE) and point-of-use (POU) technologies (Rockafellow-Baldoni et al. 2018). These As-removal filters are becoming increasingly popular as effective conter-measures for reducing microorganisms and hazardous chemicals from drinking water. An endearing feature of POE and POU devices is the facility to use on existing plumbing structures present in single houses, government or commercial buildings and facilities (Alsulaili, Al-Harbi, and Elsayed 2020; Nriagu et al. 2018).

It is noteworthy that adsorbents with high efficacy, low cost, and high selectivity are urgently required to be explored in order to meet the demand of As treatment. Accordingly, layered doubled hydroxides (LDHs) are anionic clays with counter-anions in the interlayer space and positively charged host layers which were found to exhibit high potential for effective removal of As. Further, silver nanoparticles (AgNPs) display low toxicity when compared to other nanometallic compounds, wide microbicidal actions, and are easily incorporated in low-cost materials for application in POU filters (Praveena and Aris 2015). Therefore, LDHs were widely explored for practical application in filters, and AgNPs are already

mainly designed for POU systems (Figoli, Dorraji, and Amani-Ghadim 2017). Thermodynamic investigations suggested that zero-valent iron possesses high adsorption capacity for As(V) and As(III), also considered an effective material for removal of As (Bang et al. 2005; Meng et al. 2001). Tailored bio  chars, modified geomedia, and Fe-impregnated granular activated carbon display slow uptake rates, thus their application in POU systems is still limited (Wang et al. 2020a). These adsorbent technologies do not require hazardous desorption agents and enable easy maintenance of the adsorption system.

Earlier investigators showed the effectiveness of POE and POU water treatment filters in As uptake and improvement of drinking water safety (Spayd, Robson, and Buckley 2015; Yang et al. 2020). POE filters are typically installed after the pressure tank and treat raw water, hence ensuring that all faucets are receiving treated water. In contrast, POU systems represent a smaller-scale version, treating only one tap of the home while the remaining taps have untreated water (Yang et al. 2020). Thus, POE technology is considered the most protective physical intervention for As treatment.

A biomonitoring study performed in private wells of New Jersey evaluated the performance of POE and POU in order to compare overall exposure reduction of As via both technology devices. The results obtained through collection of raw and treated water samples demonstrated that POE and POU systems effectively decreased As levels in water from approximately 120 µg/L to below 3 µg/ L (Spayd, Robson, and Buckley 2015). Further, urine samples were collected from 49 subjects to confirm the findings. Although both water treatment devices reported a consistent reduction in metalloid concentrations, the whole-house POE technology decreased urinary inorganic-related As to significantly lower concentrations than single-tap POU filter (Spayd, Robson, and Buckley 2015). However, it is worthwhile noting that POE treatment device costs approximately 8-fold more than POU system. Considering that As is classified as a human carcinogen, the additional cost may be justified (Spayd, Robson, and Buckley 2015).

4.1.2 Ion exchange system

The ion exchange system is also highlighted as a valuable technique for removing As from water. In this physicochemical process, ions are swapped between a solid resin phase and a solution phase. Synthetic resins absorb metalloid ions consistently and have been used as the solid phase for the treatment of contaminated water (US Epa 2015; Sarkar and Paul 2016).

As part of the United States Environmental Protection Agency's (US EPA) Arsenic Treatment Demonstration Program, Chen et al. (2020) investigated the performance of a full-scale ion exchange technology in water from different wells. Results demonstrated that As was effectively removed from drinking water supplies by coupling ion exchange with strong base anionic resins. However, various factors may affect the efficiency of ion exchange technology, including co-occurring contaminants, As concentration, pH, and resin type. For example, Chen et al. (2020) noted that a chromatographic peaking of As due to the presence of sulfate and more preferred anions, thus interfering in the efficiency removal of the metalloid. Despite the efficacy of ion exchange system in reducing As, additional studies may be warranted in order to explore the most appropriate resin type and parameters of this technology, also taking into account operational cost, maintenance, and capital investment (Sorg, Wang, and Chen 2014).

4.1.3 Membrane filtration

Membrane filtration processes also contribute substantially to the efficient removal of As from water. Membranes are typically synthetic materials composed of pores which allow specific constituents of a mixture to pass through them while retaining other constituents, thus acting as selective barriers (US Epa 2000). The 4 most popular membrane filtration processes include microfiltration (membrane pore size 0.1–10 μm), ultrafiltration (membrane pore size 0.01–0.1 μm), nanofiltration (membrane pore size 0.001–0.01 μm), and reverse osmosis (membrane pore size 0.0001 μm) (Choong et al. 2007; Sarkar and Paul 2016).

Microfiltration and ultrafiltration are low-pressure-driven separation techniques typically applied for the removal of organic matter, suspended particles, macromolecules, and colloids of water and groundwater. Conversely, previous investigators reported that both procedures are not suitable for an

efficient soluble As removal, since membranes are based upon pore flow model and enable multivalent ions to pass through the membrane pores, thereby showing limited capacity for metalloid treatment (Sarkar and Paul 2016). Thus, the efficiency of As removal from water might increase through a hybrid system of adsorption and microfiltration/ultrafiltration (Wan et al. 2020).

Nanofiltration (NF) is a high-pressure procedure able to remove an appreciable level of As from contaminated water (Singh et al. 2015). It is noteworthy that NF membranes are able to remove As(V) in a more efficient manner from natural waters when compared to As(III). Thus, a pre oxidation process in which As(III) might be effectively oxidized to As(V) is required. Recently, Figoli et al. (2020) examined the application of nanofiltration for remediation of As(V) from contaminated groundwater using a lab pilot unit. Data demonstrated that membranes led to an As concentrations lower than 10 pbb for groundwater, with metalloid levels ranging from 59 to 118 pbb (Figoli et al. 2020) affirming nanofiltration as a suitable technique for As(V) removal from natural water.

Finally, reverse osmosis is a well-known process based upon membrane separation for reducing various solutes and ionic species from water. A prior pilot study showed that the technique markedly removed 80–99% of As(V) from water (Schmidt et al. 2016), and was successfully applied for the treatment of As extraction, but only from model solutions. Thus, the efficiency of reverse osmosis in treating real-world contaminated sources requires further exploration (Figoli et al. 2020). Evidence suggests that the membrane filtration process may be coupled with other strategies in field conditions, including POE and POU devices, as an attempt to improve the effectiveness of water treatment (Chen et al. 2020; Yang et al. 2020).

Recent work performed in private residential wells of Maine and New Jersey evaluated the efficacy of household As treatment systems considering point-of-entry and point-of-use reverse osmosis (POU RO) systems (Yang et al. 2020). Both systems were found to diminish well water As concentration by up to two orders of magnitude. In Maine, the metalloid concentration of untreated well water was lowered from71.7 μg/L to 0.8 μg/L after treatment through the use of POU RO filter. In New Jersey, the As in private well water was decreased from 8.6 μg/L to

0.2 μg/L after using POE filters (Yang et al. 2020). Thus, data indicated that POE technology performed slightly better than POU RO system, but noted that both strategies are promising candidates to reduce As in drinking water to acceptable levels.

## 4.2 BIOLOGICAL TREATMENT

Cyanobacteria and algae species have developed several mechanisms for As transformation pathways, including As(III) oxidation and methylation (Ye et al. 2012), As(V) reduction (Wang et al. 2015), and arsenolipid and arsenosugar biosynth esis (Xue et al. 2017). Despite the toxicity of aqueous As in environment, these organisms are tolerant against high levels of the metalloid and drawn considerable attention as promising alternatives for As remediation programs (Zhu et al. 2020).

*Leptolyngbya boryana* is a typical filamentous cyanobacterium widely distributed in freshwater environment, which demonstrates powerful abilities for accumulation and tolerance of As. Zhu et al. (2020) examined the use of L. boryana biogeochemical cycle with respect to the metalloid. L. boryana exhibited multiple pathways of As biotransformation, such as As(V) reduction, As(III) oxidation, methylation, and arsenosugar and arsenolipid biosynthesis under lab conditons suggesting a critical role for As treatment in aquatic environments (Zhu et al. 2020).

Recently investigators reported on the ability of the cyanobacterium *Nostoc* to accumulate As in cells (Patel, Tiwari, and Prasad 2018; Xue et al. 2017). The nitrogen-fixing *Nostoc sp*. is a typical filamentous organism ubiquitous in freshwater ecosystems. Xue et al. (2017) found that *Nostoc sp*. was able to produce two species of arsenosugar phospholipids and a phosphate arsenosugar (Oxo-PO4), and demonstrated a mechanism of demethylation, thus presenting multiple species of arsenic biotransformation pathways cooccurring in the species. These findings provide novel insights into the function of *Nostoc sp*. in As biogeochemical cycle. Further, the intracellular metalloid accumulation was also investigated in *Nostoc muscorum*, and data confirmed that the diazotrophic cyanobacterium was able to bioaccumulate both As(III) and As(V) (Patel, Tiwari,

and Prasad 2018). Evidence demonstrated that intracellular accumulation of As in As(III) species treated cells was higher in comparison to As(V) species indicative of a more toxic nature of As(III). Further, Patel, Tiwari, and Prasad (2018) found that survival of *Nostoc muscorum* after high As accumulation in the cells indicated that this species may be used as a promising organism for bioremediation of As from contaminated aquatic systems.

*Microcystis aeruginosa* has also been identified as a potential algae species for bioremediation and removal of heavy metals from water. Previously Wang et al. (2015) reported the potential of *M. aeruginosa* for detoxifying As through accumulation, methylation, or transformation to less toxic inorganic species. In fact, *M. aeruginosa* is widely found in freshwater ecosystems, often containing high internal concentrations of As, hence suggesting that the bloom algae is able to accumulate this pollutant. It is of interest that Wang, Luo, and Yan (2013) noted the active uptake of As(III) and As(V) after 15-days of exposure to *M. aeruginosa* cells. This accumulation of As rose with increasing arsenite and arsenate concentrations in the exposure test (Wang, Luo, and Yan 2013).

In addition to As contamination in groundwater, phosphorus is one of the major limiting factors in aquatic ecosystems. The presence of this element leads to eutrophication due to overload, therefore damaging the water ecosystem (Conley et al. 2009). Luo et al. (2020) investigated the effects of arsenate on Microcystis species under different phosphorus regimes. Microcystis displayed a potent ability to absorb phosphorus from the environment. The results showed that reactive oxygen species (ROS) elimination by Microcystis was a remarkable As(V) detoxification mechanism. Alterations of enzymes activities also confirmed the efficient detoxifying mechanisms of M. aeruginosa by synthesizing enzymatic and non-enzymatic antioxidants to control ROS (Luo et al. 2020).

## 4.3 NANOPARTICLES AND NANOCOMPOSITES FOR WATER TREATMENT

Considering that As is a ubiquitous metalloid responsible for initiating acute poisoning and/or chronic toxicity, the development of innovative technologies for As removal from wastewater is of critical importance. It is noteworthy that conventional systems such as electrodialysis, coagulation/ co-precipitation, and

chemical precipitation are available for remediation of As contaminated groundwater. However, these techniques have sub-optimal efficiency and require high initial and maintenance costs, and are financially not feasible mainly in developing countries (Asere, Stevens, and Laing 2019; Ashraf et al. 2019). Hence, adsorption still remains as a promising approach owing to the low cost, safe to handle, suitable operation, and high efficiency even at low concentrations of metalloid (Lata and Samadder 2016). It is estimated that this technique, when compared to conventional systems, reduces capital costs by approximately 20%, operational costs by 36%, and total treatment costs by 28% (Asere, Stevens, and Laing 2019). However, the adsorption capacity of traditional sorbents is limited by the irregular pore structures and chemical properties of these compounds (Veličković et al. 2012).

Metal-organic frameworks (MOFs) are emerging class of novel adsorbents that have been widely used in different applications, such as selective capture and storage of gases, transferring of medicine in the individual's body, and for pollutants removal from the environment, including fluoride (Lin, Liu, and Chen 2016), phosphorus (Shams et al. 2016), chromium (Sheng et al. 2016) and As (Massoudinejad et al. 2018).

Regarding the nano-scaled adsorbents, zeolitic imidazolate frameworks (ZIFs) constitute wellknown building blocks for MOFs. ZIF nanoparticles are porous crystalline polymers with tetrahedral network formed by organic imidazolate ligands and zinc ions (Evans et al. 2020). In addition to the high stability in water, a striking feature of these frameworks is chemical robustness, ultrahigh porosity, and thermal stability (Park et al. 2006; Wang et al. 2008).

4.3.1 Zeolitic imidazolate framework-8

Based upon the use of crystalline microporous zeolites for water treatment, softening, and purification, ZIF-8 nanoparticles were investigated as an attractive sorbent for As removal. Previously Jian et al. (2015) assessed the performance of As capture and adsorption by ZIF-8 nanoparticles. After the synthesis via a facile approach at room temperature, ZIF-8 nanocrystals demonstrated rapid adsorption of arsenite and arsenate at the beginning, indicating that the adsorption rate

constant of As(V) is approximately 4-fold greater than that of As(III), and then quickly levels off. Considering the effect of pH, Jian et al. (2015) reported that ZIF-8 nanoparticles dissolved into water under acidic conditions, thereby leading to decline of adsorption capacity of the nanoparticles. Subsequently, the optimal pH for As adsorption on ZIF-8 was achieved at neutral condition, suggesting ZIF-8 nanostructures as a promising candidate for the adsorption of As(III) and As(V) (Jian et al. 2015).

## 4.3.2 Nanocrystalline titanium dioxide and copper oxide nanoparticles

Titanium-based nanocomposite materials have also been examined as potential alternatives to remove As. Titanium dioxide (TiO2) exhibits low toxicity, low cost, chemical and physical stability, and high affinity for As(III) and As(V) (Saravanan et al. 2013). In a pilot study Liu, Zuo, and Vecitis (2014) determined the performance of a TiO2- coated carbon nanotube network filter for removal of As from water. The findings showed that groundwater samples containing 44 ppb As were treated after a single-pass filtration indicating the high potential of TiO2 in treating contaminated water.

Metal oxide nanoparticles have high surface areas and several hydroxyl groups, which play an important role in pollutant removal from water. Nano-size adsorbents are emerging as potential strategies to existing conventional approaches for water and wastewater treatment (Hayati et al. 2018; Kumar, Ranjan, and Quaff 2020; Lata and Samadder 2016). In this context, it is noteworthy that copper oxide nanoparticles (CuO) performed well in the presence of competing anions and there was no need for pH adjustments or oxidation of As(III) to As(V) (Martinson and Reddy 2009). Reddy, McDonald, and King (2013) examined the performance of CuO nanostructures as metal-based adsorbents to remove As from groundwater. Batch adsorption kinetics experiments assessed the uptake of As by nanoparticles and exhibited a high effectiveness in filtering the pollutant from the groundwater. In addition, continuous flow  through experiments indicated the potential in developing a practical one-step process for field applications to remove metalloid from natural water (Reddy, McDonald, and King 2013). Further, the removal of As(III) from contaminated water was recently

investigated with the synthesis of CuO nanoparticles (Kumar, Ranjan, and Quaff 2020). Data showed that 97.8, 94.6, 91.5, and 88.4% of arsenite was removed from an initial concentra⬚tion of 100, 200, 500, and 1000 µg/L, respectively. Although the cost-effectiveness is still a hurdle to be overcome for the widespread use of CuO nanoparticles, this study also found that the cost of lab synthesis of CuO NPs was far less than commercially available CuO nanoparticles (Kumar, Ranjan, and Quaff 2020). Certainly, nano-size adsorbents need to continue to be explored in order to establish an effective and safe approach to achieve maximal adsorption properties of metal oxides nanoparticles.

## 5 CONCLUDING REMARKS

In conclusion, the presence of As in natural water is driving the exploration of both physico-chemical and biological treatment systems attributed to dangers associated with metalloid exposure. This has consequently led to the development of nanoparticles that efficiently reduce or remove water-borne As. Arsenic is widely dispersed into water due to natural and anthropogenic activities, such as weathering process, agricultural pesticides, and mining, and the provision of clean water remains a hurdle for scientists and engineers. Alarmingly, long-term use of As-contaminated water has been associated with several debilitating diseases. Thus, scientific evidence indicates the approaches mentioned as effective and sustainable technologies for removing As species from groundwater and drinking water. Sustainable As treatment alternatives have yet to be explored, and further investigation is still required to achieve higher removal performance of metalloid.

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# CHAPTER 2. PHYTOREMEDIATION, BIOACCESSIBILITY AND ECOTOXICOLOGICAL RISK ASSESSMENT OF ARSENIC IN A GOLD MINING AREA

## ABSTRACT

The physicochemical and biological parameters of aquatic ecosystems are directly affected by mining activities, increasing the ecotoxicological risk related to exposure to contaminants and pollutants. In this study, a floating aquatic macrophyte was used in a gold mining area as a model organism to assess the environmental risk and its potential application in bioremediation of heavy metals. The physicochemical parameters of water and sediments were evaluated, as well as the phytoremediation parameters (bioconcentration and translocation factors) of *Hydrocotyle ranunculoides* L. The results showed a significant bioconcentration of Cr, Pb, Cu, and Zn in the roots of the macrophyte (high BCF: As>Cu>Zn>Pb>Cr), confirming its suitability for use in rhizofiltration. Regarding arsenic bioconcentration, *H. ranunculoides* demonstrated a high BCF and TF >1, indicating its phytoextraction potential, an essential requirement for plants to be used in bioremediation programs.

**Keywords:** Ecotoxicology; aquatic macrophyte; sediments; heavy metals; bioremediation.

# 1 INTRODUCTION

Current economic development policies have intensified the use of water resources, threatening the supply of drinking water (Selvaraj and Velvizhi, 2021; Erasmus et al., 2020). Mining is one of the most aggressive and polluting activities to aquatic ecosystems, strongly affecting water bodies, resulting in significant decreases in water quality due to large amounts of hazardous waste, such as solid residues and harmful effluents to the environment (Beck et al., 2020; Clark et al., 2021; Gigantone et al., 2020).

The contamination of water resources by mining operations occurs due to heavy metals contained in mining waste (Sasmaz et al., 2021). These contaminants pose a threat to human health and aquatic biota owing to the persistent characteristic and bioaccumulation potential of toxic compounds in the natural environment (Agarwal et al., 2022).

When dispersed in water sources, heavy metals are temporarily immobilized in the sediment by absorption, co-precipitation, and hydrolysis processes, transforming this compartment into sinkholes (Haynes and Zhou, 2022). However, environmental changes can mobilize metals accumulated in sediments into the water column. When bioavailable, metals can progressively accumulate from one trophic level to another along the food chain (biomagnification), damaging ecosystems and, consequently, affecting human and environmental health (Agarwal et al., 2022).

The versatility and bioavailability of metals in water or sediments are related to the chemical composition of each metal. Natural environmental variables, such as pH fluctuations, redox potential and organic matter content, influence the availability and storage capacity of sediments, thus promoting their mobility in

aquatic ecosystems. Additionally, the toxicity and versatility of heavy metals in sediments depend on their total concentration and state of matter. Therefore, some metals can display different chemical structures – water soluble, exchangeable, bound to organic matter, bound to iron, aluminium, and manganese oxides/hydroxides, carbonates, phosphates, sulphates and other secondary minerals (Brito et al., 2020; Jha and Tripathi, 2021).

Previous investigations have discovered the benefits of using biological systems to remediate waste as a natural alternative (Hou et al., 2020; Sun et al., 2020). Notably, the use of macrophytes in bioremediation is a low-cost and sustainable strategy to recover affected environments, reducing the bioavailability of contaminants in aquatic environments (Bhat et al., 2022; Shikha and Singh, 2020). Aquatic macrophytes represent a diverse group of plants distributed worldwide in different ecosystems (Jeelani et al., 2017). These photosynthetic organisms display several characteristics favorable to the absorption of contaminants and, consequently, to their use in phytoremediation processes, due to the efficient absorption of contaminants by their roots, resilience to adverse ecological and toxicity factors, high reproductive capacity, and high potential for biomass accumulation (Bramhanand and Laxminarayana, 2021; Vasconcelos et al., 2021; Timalsina et al., 2022).

Intrinsically, the phytoremediation process not only removes contaminants from the environment but also potentially converts them into less toxic compounds, restoring water quality parameters within the permissible limits of environmental protection agencies (Lakra et al., 2019; Tufail etl al., 2022). Thus, this study aimed to evaluate the phytoremediation potential of the floating aquatic macrophyte

*Hydrocotyle ranunculoides* L. for heavy metals in a gold mining area, located near an urban environment, through an ecotoxicological risk assessment.

## 2 Material and Methods

### 2.1 Studied sites

The sampling sites are located in the Conceição River and Santa Bárbara River, in the Quadrilátero Ferrífero region – Southeastern Brazil, known worldwide for the abundance of gold and iron of its Precambrian terranes (Baltazar and Zuchetti, 2005; Teixeira et al., 2020), which directly impacts water quality due to the massive mineral resource extraction (Figure 1). To assess the impacts of environmental contamination, five points were established – each with their respective samples of water, sediments, and macrophytes (Figure 2). The reference point was located upstream of the mining waste disposal area and close to a Permanent Preservation Area (PPA). Site 1 is also located upstream of the mining area, but further away from the reference point. Sites 2, 3 and 4 are downstream of the mining area and closer to urban centers.



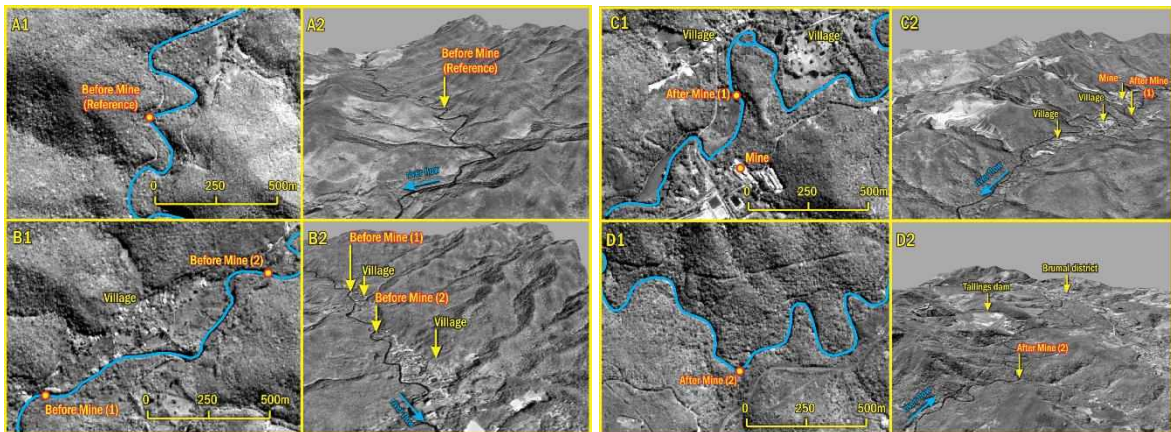**Figure 1.** Location map of the study area.

**Figure 2.** Distribution of sampling sites at Conceição River and Santa Bárbara River in Southeastern Brazil.

## 2.2 Heavy metal content in sediments, water, and macrophyte

Sediment, water, and plant samples were collected during the transition period from the wet to the dry season in May 2021. Five sediment samples (100 cm$^3$) were collected at the different sampling sites (depth = 10 cm) to quantify the composition of As, Cr, Pb, Cu and Zn. The samples were transferred to the analytical laboratory in amber glass bottles. Then, the sediment samples were treated with nitric acid (HCl 37% and HNO$_3$ 70%, 3:1 v/v) following the ISO 11466:1995 protocol (ISO, 1995).

Water samples (n=5) were also collected from the five investigated sites. Physicochemical parameters and heavy metal concentration were determined according to the Guidelines for the Examination of Water and Wastewater (APHA-AWWA-WPCF, 2005).

Five samples from the native species *Hydrocotyle ranunculoides*, used as an ecotoxicological bioindicator at the area of study, were collected from each sampling site. Foraged plants were transported to the laboratory in plastic bags.

Then, the plant samples were washed with tap water to remove sediment particles and rinsed with distilled water. The roots and shoots were separated and dried for 72 hours at 68 ºC. Afterwards, the dried tissues were grounded into a powder and submitted to digestion procedures using a concentrated nitric-perchloric acid solution ($HNO_3$-$HClO_4$) in a 3:1 ratio.

The suspensions obtained from each sediment, water and plant samples were determined by Flame Atomic Absorption Spectrometry (FAAS).

## 2.3 Phytoremediation indicators

The phytoremediation indicators (bioconcentration factor – BCF and translocation factor – TF) related to the heavy metal content were calculated according to Equations 1 and 2 (Yoon et al., 2006):

$$BCF = [metal]\ roots\ (mg.kg^{-1}) / [metal]\ water\ (mg.L^{-1}) \qquad (1)$$

$$TF = [metal]\ shoots\ (mg.kg^{-1}) / [metal]\ roots\ (mg.kg^{-1}) \qquad (2)$$

## 2.4 Toxicity parameters

The total bioconcentration of metals in the whole plant was evaluated using reference values for species in general, on a dry weight basis (Kabata-Pendias and Pendias, 2001).

## 3 RESULTS

The physicochemical parameters indicated that, from the reference site, the water samples collected downstream showed higher concentrations of contaminants typical of industrial and domestic effluents (fecal coliforms, nitrates,

nitrites, total phosphorus, and ammonia nitrogen) and an increase in total solids and turbidity (Table 1).

According to Figure 1 and 2, it is possible to infer that polluting discharges from mining operations are added to urban effluents discharged directly into watercourses. Importantly, both sources of pollution affect the environment and exposed organisms.

Heavy metal concentrations (As, Cr, Pb, Cu and Zn) were determined in sediments, water, and plant environments (Table 2). The experimental results revealed a significant increase in the concentrations of As, Cr, Pb, Cu and Zn in the sediment samples at the sites downstream of the reference point. Moreover, Cr concentration was above the legal environmental standards at all sampling sites. As and Cu levels also exceeded the legal limits, but only at site 4. In water samples, only the As concentration (at the reference site and site 1) and the Zn concentration (at the reference site) did not exceed the mandatory limits of the environmental legislation, thus indicating high bioavailability of pollutants to biota.

Table 2 depicts the phytoremediation indicators BCF and TF. The highest BCF of *H. ranunculoides* was observed for As, followed by Cu, Zn, Pb, and Cr. These findings indicate a crucial role of the species in bioconcentrating metals in contaminated environments, as in the studied region.

Regarding the ability to translocate metals from the roots to the shoots (translocation factor), *H. ranunculoides* presented TF > 1 only for As. This result demonstrates the high rhizofiltration potential of the macrophyte to maintain Cr, Cu, Pb and Zn on its root system and a high capacity of As bioaccumulation in its biomass (phytoextraction).
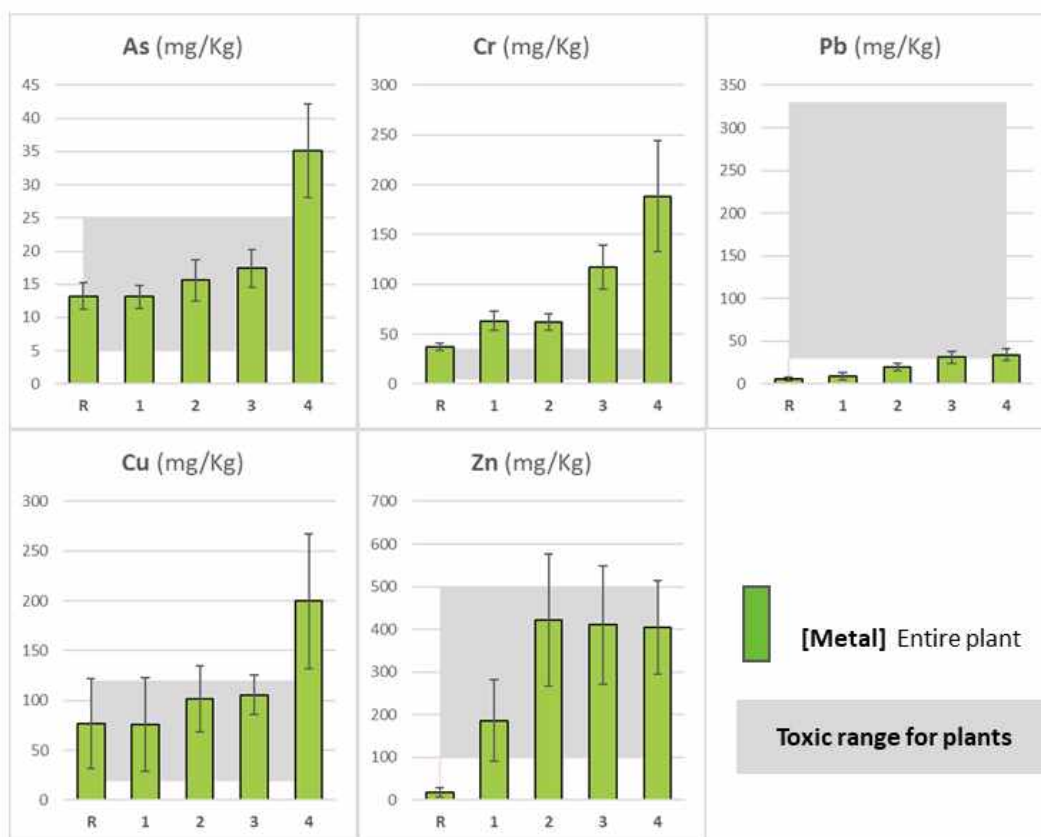
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**Figure 3**. Mean (± SD) concentrations of metals in entire plant and reference values for toxic range for plants.

Figure 3 illustrates the metal concentrations in the whole plant in relation to the toxic range for plants (Kabata et al., 2001). The results highlight the metal accumulation potential of *H. ranunculoides* in its biomass, especially As, and its ability to develop even in a toxicologically hostile environment for plants.

**Table 1.** Mean (± SD) concentrations of physico-chemical and pollution-related parameters obtained from reference and sampling sites

| PARAMETERS | Reference X (± SD) | Site 1 X (± SD) | Site 2 X (± SD) | Site 3 X (± SD) | Site 4 X (± SD) |
|---|---|---|---|---|---|
| Dissolved oxygen (mg/L) | 8.33 (± 0.51)a | 7.23 (± 0.15)a | 6.87 (± 0.21)a | 7.37 (± 0.38)a | 7.30 (± 0.25)a |
| Temperature (°C) | 18.30 (± 0.36)a | 18.43 (± 0.40)a | 19.43 (± 0.25)a | 19.47 (± 0.55)a | 19.27 (± 0.21)a |
| Conductivity (µS/cm) | 9.63 (± 0.76)a | 11.03 (± 1.37)a | 16.73 (± 3.53)b | 26.33 (± 6.02)b | 120.07 (± 18.49)c |
| Chlorides (mg/L) | 1.07 (± 0.15)a | 1.20 (± 0.20)a | 1.40 (± 0.26)a | 1.37 (± 0.15)a | 4.21 (± 1.24)b |
| Fecal coliforms (NMP/100mL) | 66.67 (± 11.02)a | 119.00 (± 22.07)b | 188.33 (± 99.60)b | 402.67 (± 139.92)b | *4781.33 (± 250.50)c |
| pH | 6.67 (± 0.40)a | 7.27 (± 0.45)a | 7.63 (± 0.15)a | 7.13 (± 0.15)a | 7.00 (± 0.26)a |
| BOD (mg/L) | 1.07 (± 0.06)a | 1.20 (± 0.10)a | 1.30 (± 0.10)a | 1.13 (± 0.16)a | 1.73 (± 0.32)a |
| Nitrates (mg/L) | 1.47 (± 0.21)a | 1.70 (± 0.26)a | 1.90 (± 0.20)a | 2.97 (± 0.68)b | 4.50 (± 0.60)b |
| Nitrites (mg/L) | 0.01 (± 0.00)a | 0.023 (± 0.015)a | 0.033 (± 0.006)a | 0.047 (± 0.01)b | 0.057 (± 0.025)b |
| Total phosphorus (mg/L) | ND | 0.013 (± 0.006)a | 0.018 (± 0.003)a | 0.043 (± 0.01)b | 0.062 (± 0.008)b |
| Turbidity (UNT) | 6.33 (± 1.53)a | 7.67 (± 1.15)a | 12.33 (± 1.53)b | 14.67 (± 2.08)b | 36.33 (± 4.163)c |
| Total solids (mg/L) | 26.43 (± 14.33)a | 34.70 (± 15.90)a | 59.93 (± 10.70)a | 68.73 (± 10.46)a | 113.87 (± 25.50)b |
| Ammonia Nitrogen (mg/L) | 3.49 (± 0.06)a | 3.94 (± 0.062)a | 3.500 (± 0.082)a | 4.55 (± 0.07)a | 4.87 (± 0.134)b |
| Altitude | 798.32 | 770.11 | 761.20 | 758.45 | 733.98 |

ND: Not detected above detection threshold of 0.001 mg/L. *Concentrations above the limit permitted by the CONAMA Resolution 357/2005 (Brasil, 2005).

Means followed by the same letter within a line are not significantly different. (Tukey's test; 95% confidence level).

**Table2.** Metal analysis (sediments, water and *H. rannculoides*) and phytoremediation indexes [bioconcentration fator (BCF) and translocations fator (TF)].

| Metal | Site | Sediment (mg/Kg) | Water (mg/l) | *Hydrocotyle ranunculoides* | | | |
|---|---|---|---|---|---|---|---|
| | | | | root | shoot | BCF (r/w) | TF (s/r) |
| As | R | 7.2 (± 1.3) | 0.01 (± 0.01) | 6.1 (± 1.4) | 7.3 (± 2.2) | 588.6 (± 85.6) | 1.1 (± 0.1) |
| | 1 | 7.4 (± 1.2) | 0.01 (± 0.01) | 6.0 (± 1.7) | 7.4 (± 2.6) | 570.3 (± 98.8) | 1.2 (± 0.1) |
| | 2 | 9.2 (± 4.3) | *0.02 (± 0.01) | 7.4 (± 2.1) | 8.5 (± 2.0) | 587.0 (± 105.4) | 1.1 (± 0.1) |
| | 3 | 10.5 (± 4.7) | *0.02 (± 0.01) | 8.1 (± 1.9) | 9.3 (± 2.6) | 618.2 (± 88.7) | 1.2 (± 0.1) |
| | 4 | *30.3 (± 4.5) | *0.03 (± 0.01) | 16.1 (± 2.3) | 17.8 (± 3.7) | 565.6 (± 138.9) | 1.3 (± 0.1) |
| Cr | R | 87.3 (± 15.4) | *0.9 (± 0.2) | 30.4 (± 4.5) | 9.0 (± 2.3) | 33.0 (± 3.2) | 0.3 (± 0.1) |
| | 1 | *104.1 (± 17.9) | *1.3 (± 0.5) | 47.2 (± 15.8) | 15.8 (± 4.5) | 34. 4 (± 5.9) | 0.3 (± 0.1) |
| | 2 | *102.2 (± 37.8) | *1.3 (± 0.3) | 46.8 (± 14.7) | 15.3 (± 3.7) | 35.6 (± 4.7) | 0.3 (± 0.1) |
| | 3 | *199.4 (± 77.3) | *2.55 (± 0.4) | 87.3 (± 14.8) | 28.8 (± 7.3) | 34.5 (± 5.8) | 0.3 (± 0.1) |
| | 4 | *404.7 (± 136.3) | *4.59 (± 0.3) | 133.9 (± 26.8) | 46.2 (± 11.7) | 35.1 (± 4.6) | 0.3 (± 0.1) |
| Pb | R | 2.5 (± 0.4) | *0.02 (± 0.01) | 2.9 (± 1.1) | 1.3 (± 0.5) | 145.3 (± 34.4) | 0.4 (± 0.1) |
| | 1 | 4.8 (± 1.1) | *0.05 (± 0.05) | 6.3 (± 1.2) | 2.8 (± 0.7) | 121.9 (± 19.7) | 0.4 (± 0.1) |
| | 2 | 10.6 (± 2.1) | *0.11 (± 0.1) | 13.6 (± 3.7) | 6.0 (± 2.2) | 123.8 (± 25.2) | 0.4 (± 0.1) |
| | 3 | 15.4 (± 2.3) | *0.17 (± 0.1) | 21.4 (± 4.3) | 7.9 (± 2.1) | 122.7 (± 31.4) | 0.4 (± 0.1) |
| | 4 | 16.7 (± 2.0) | *0.19 (± 0.1) | 22.3 (± 3.8) | 9.8 (± 1.8) | 116.7 (± 28.7) | 0.4 (± 0.2) |
| Cu | R | 10.3 (± 2.2) | *0.13 (± 0.1) | 55.0 (± 33.4) | 22.7 (± 18.4) | 423.4 (± 112.7) | 0.4 (± 0.2) |
| | 1 | 15.5 (± 8.9) | *0.15 (± 0.1) | 55.8 (± 34.2) | 22.3 (± 16.8) | 388.4 (± 123.5) | 0.4 (± 0.2) |
| | 2 | 77.7 (± 16.8) | *0.16 (± 0.09) | 70.3 (± 22.7) | 31.3 (± 14.6) | 490.2 (± 101.3) | 0.4 (± 0.2) |
| | 3 | 78.1 (± 23.7) | *0.15 (± 0.09) | 72.4 (± 17.3) | 32.8 (± 12.7) | 484.4 (± 88.3) | 0.4 (± 0.1) |
| | 4 | *154.2 (± 38.3) | *0.28 (± 0.1) | 140.2 (± 37.6) | 61.3 (21.3) | 515.3 (103.2) | 0.4 (0.1) |
| Zn | R | 23.1 (± 4.8) | 0.08 (± 0.02) | 13.2 (± 7.3) | 5.4 (3.6) | 162.8 (88.2) | 0.4 (0.2) |
| | 1 | 40.5 (± 12.4) | *0.72 (± 0.3) | 110.2 (± 54.8) | 77.3 (42.2) | 157.5 (71.4) | 0.7 (0.4) |
| | 2 | 68.9 (± 22.8) | *1.66 (± 0.4) | 255.3 (± 82.4) | 167.3 (77.1) | 153.3 (62.9) | 0.6 (0.4) |
| | 3 | 72.5 (± 21.3) | *1.67 (± 0.4) | 249.9 (± 67.8) | 160.3 (55.2) | 146.0 (51.4) | 0.6 (0.3) |
| | 4 | 73.1 (± 14.7) | *1.77 (± 0.3) | 252.4 (± 58.7) | 154. 2 (42.0) | 139.7 (48.3) | 0.5 (0.2) |

* Above the values established by the CONAMA Rresolution CONAMA 344/04 for sediment and CONAMA 357/2005 for water.

**4 Discussion**

The physicochemical analysis showed that water pH was close to all sampling sites, thereby contributing to keep the metals in the precipitation form, with less mobility of sediment to water (Souza, 2015). However, due to the pedological characteristics of the region and the influence of industrial and domestic waste disposal, there was acidification of the environment at the different sites.

Regarding Cr and Cu concentrations, although these metals showed significant values that exceed the environmental standards, indicating pollution in the studied environment, they are less available to biota, as they tend to preferentially bind to Fe and Mn oxides, in addition to forming complexes with organic matter. Similarly, Pb also tends to form complexes with organic matter (ATSDR, 200; 2007; Jennings et al., 2008).

Specifically, the increase in Cu concentration caused by mining activities directly affects the environment. Although copper has a natural mineral origin (CuFeS), its exposure to aquatic environments allows oxidation, leading to metal dissolution (Peng et al., 2009). Anthropogenic activity both in mining and domestic effluent disposal tends to intensify pollution and ecotoxicological risks, since Cu levels increase with greater availability of organic matter in acidified environments (Baltazar and Zuchetti, 2005).

Zn concentration indicates natural lithogenic influence, since this metal is often found in nature as sulphide associated with lead, silver, and iron, with lower bioavailability (Maycock et al., 2008). Nevertheless, based on the granulometric analysis of sediment, a recent study revealed the predominance of fine particles (<63 μm) in the investigated region, especially clay and silt, recognized for their

notable ability to transport metals attached to minerals in water bodies (Marques et al., 2019).

The occurrence of arsenic is justified not only by the geo-chemical local nature (oxidation of auriferous sulphide ores) but also by the disposal of mining debris. Therefore, the results of physicochemical analysis reveal an environment with a high potential toxicological risk of heavy metals, in which the natural occurrence of gold with arsenopyrite adds to the impacts of mining and urbanization activities, increasing the availability of metals, mainly As (Quináia, 2006).

It is worth noting the impact of urban sewage disposal into the river, downstream of the mining area, as the presence of fine particles, organic matter, and acidification of the environment tend to favor the availability of metals in aquatic ecosystems. The bioavailability of these elements is directly associated with increased toxicity due to the bioaccumulation and biomagnification of pollutants in biota (Thanh-Nho et al., 2019; Verhaert et al., 2019).

Mining products and waste produce arsenic-rich effluent that can accumulate large amounts of contaminants in aquatic ecosystems (Ali et al., 2019; Teixeira et al., 2020). Monteiro de Oliveira et al. (2020) state that pollution resulting from mining, especially with arsenic, can be found in the North, South, and Southeast regions of Brazil and in different countries such as Argentina, Bangladesh, China, United States, Myanmar, and Pakistan.

Understanding the dynamics of environmental contamination and bioavailability of metals in water must go beyond the classic approach that only considers the permissible limits of physicochemical parameters. Importantly, water-sediment compartments interchange contaminants, directly affecting biota

due to the occurrence of biomagnification and bioaccumulation (Affandi and Ishak, 2019; Bergmann and Graça, 2020; Marrugo-Negrete et al., 2020; Chormare and Kumar, 2022). Considering the low biodegradability and high toxicity of metals for biota, the use of native plant species with decontamination potential is a promising biotechnological approach (Demarco et al., 2018; Eid et al., 2020; Hejna et al., 202; Del Río et al., 2022).

The results of this study reinforce the potential and advantages of using *H. ranunculoides* in phytoremediation strategies. Lastly, for investigating the use of a native and adapted species and considering the bioaccessibility and ecotoxicological risk assessment of arsenic and other metals in a gold mining area, these findings are relevant and contribute to planning, monitoring, bioremediation, and environmental preservation actions.

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