The purpose of wastewater treatment is water reuse. It reduces potable water consumption while preventing fresh water contamination. Water reuse schemes have already been successfully established in different locations. Treatments using constructed wetlands are widely studied as a more economical and environmentally-friendly alternative for treating wastewater. In these systems, the control of inorganic species is also important. This study monitored cations (Na\(^+\), K\(^+\), Li\(^+\) and NH\(_4^+\)) and anions (SO\(_4^{2-}\), NO\(_3^-\), NO\(_2^-\), Cl\(^-\) and PO\(_4^{3-}\)) in a constructed wetlands (CWs) system, a rainwater catchment system, sewage treatment system, and in final reuse water. The monitoring was accomplished using ion chromatographic analysis. The removal values found in the CWs were: 99.9% K\(^+\), NH\(_4^+\) and SO\(_4^{2-}\), 52.6% Na\(^+\), 89.8% NO\(_3^-\), 98.2% NO\(_2^-\), 63.6% Cl\(^-\) and 96.8% PO\(_4^{3-}\). The results also showed that CWs system is suitable for removing ions from the wastewater.

**KEYWORDS**

Reuse, constructed wetlands (CWs), wastewater monitoring, ions

**ABSTRACT:** The purpose of wastewater treatment is water reuse. It reduces potable water consumption while preventing fresh water contamination. Water reuse schemes have already been successfully established in different locations. Treatments using constructed wetlands are widely studied as a more economical and environmentally-friendly alternative for treating wastewater. In these systems, the control of inorganic species is also important. This study monitored cations (Na\(^+\), K\(^+\), Li\(^+\) and NH\(_4^+\)) and anions (SO\(_4^{2-}\), NO\(_3^-\), NO\(_2^-\), Cl\(^-\) and PO\(_4^{3-}\)) in a constructed wetlands (CWs) system, a rainwater catchment system, sewage treatment system, and in final reuse water. The monitoring was accomplished using ion chromatographic analysis. The removal values found in the CWs were: 99.9% K\(^+\), NH\(_4^+\) and SO\(_4^{2-}\), 52.6% Na\(^+\), 89.8% NO\(_3^-\), 98.2% NO\(_2^-\), 63.6% Cl\(^-\) and 96.8% PO\(_4^{3-}\). The results also showed that CWs system is suitable for removing ions from the wastewater.

**RESUMEN:** El propósito del tratamiento de aguas residuales es la reutilización del agua. Esto reduce el consumo de agua potable y previene la contaminación del agua de primer uso. La reutilización del agua ya se ha implementado con éxito en diferentes lugares. Los tratamientos que utilizan los humedales artificiales son ampliamente estudiados como una alternativa más económica y ecológica para tratar las aguas residuales. En estos sistemas, el control de especies inorgánicas también es importante. Este estudio ha monitoreado cationes (Na\(^+\), K\(^+\), Li\(^+\) y NH\(_4^+\)) y aniones (SO\(_4^{2-}\), NO\(_3^-\), NO\(_2^-\), Cl\(^-\) y PO\(_4^{3-}\)) en un sistema de humedales construido (CWs), en un sistema de captación de agua de lluvia, en el tratamiento de aguas residuales y en agua reutilizable final. El monitoreo se llevó a cabo utilizando el análisis cromatográfico de iones. Los valores de remoción encontrados en CWs fueron: 99.9% K\(^+\), NH\(_4^+\) y SO\(_4^{2-}\), 52.6% Na\(^+\), 89.8% NO\(_3^-\), 98.2% NO\(_2^-\), 63.6% Cl\(^-\) y 96.8% PO\(_4^{3-}\). Los resultados también mostraron que el sistema CWs está adecuado para la eliminación de iones del agua residual.

**1. Introduction**

Environmental problems and restrictions indicate the necessity of planned water reuse. For more than 20 years, scientists have been seeking ways to avoid the shortage of water resources and control the rising cost of drinking water [1-9].

The estimated number of people living in regions with predicted intense water scarcity in 2025 is approximately 2.7 billion people, and the volume of water will have to increase 41% to meet the needs of the population [7]. In poor countries, the problems are more alarming in relation to untreated wastewater [10].

Even though most of the farm households are aware of the environmental and health consequences related to the crop irrigation with wastewater, they still use it because of its cost advantages. This issue is one of the sanitary challenges also found at water-scarce regions [11]. This practice is widely used in Africa; for example, in [12] observed that wastewater treatment systems do not always reach enough quality for the purposes of irrigation and for non-potable applications. Therefore, water reuse might be dangerous for the farmers in some regions.
An alternative for minimizing the water scarcity is the reuse of sewage water from washing clothes and dishes as well as from showers because it is non-potable water. This procedure has already been successfully introduced in hotels [3], schools [8] and residential buildings [13].

The cost reduction of the water reuse process has been studied to find a more economic and natural method. Constructed wetlands (CWs) are an alternative ecotechnological system for small-scale communities [14].

A wastewater treatment system using CWs has minimum operating costs and may solve the problems concerning wastewater in rural areas with low incomes [15]. According to [16], CWs have been the simplest and least costly alternative for wastewater treatment in rural areas in China. These CWs are promising systems for the removal of carbon and nitrogen. However, the nitrogen removal may not be as effective due to low dissolved oxygen in wetlands. Using CWs may also be an alternative in rural domestic wastewater for phosphorus removal [17] as well as to reduce 99.9% of fecal coliforms [18].

Thus, the CWs have several advantages such as high efficiency purification, robust system, plasticity of configuration with different plant species, ability to adapt to load changes, low cost of engineering infrastructure and operation, etc. [18, 19]. Moreover, they can be integrated into productive agricultural systems. For example, better yields are reached planting rice with this system when comparing to the use of fertilizers [17].

In studies conducted in cold regions of China, the type of crop used can ensure the development of CWs systems even in cold periods [20] because the thick layer of biomass may provide thermal insulation. Otherwise, the system would be more complex requiring subsurface drainage with a greenroverse structure [21]. In [20] used a CW system with Salix babylonica and they obtained the thermal insulation. Moreover, they concluded that it is profitable, does not require energy input and it may be used in single-family homes in developing regions.

Furthermore, the coupling of an upflow anaerobic sludge blanket (UASB) prior to CWs is a promising alternative to traditional septic/sink tank systems that are widely used for domestic wastewater [22].

The vegetation choice is essential in the CWs and has the function of absorbing pollutants and transferring nutrients from microorganisms in the rhizosphere [23]. In this system, there is a combination of continuous exposure to flooding and waste streams containing a relatively high concentration and variety of pollutants [24].

Several types of vegetation have already been studied, and their absorption efficiency for many different nutrients is known [23, 25-28].

The absorbed nutrient rate by plants varies from 3 to 47% for nitrogen removal and 3 to 60% for phosphorus removal. This variation is determined by the type of plant used in the treatment and the type of effluent to be treated [26]. Several studies have demonstrated the efficacy of CW treatment with respect to fecal coliform and pathogenic micro-organism removal [3, 4]. In addition, the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) removal were approximately 80% [29]. The excessive concentration of nutrients in wastewater, particularly nitrogen and phosphorus leads to the eutrophication of water bodies (such as, lakes and rivers) and subterranean water contamination [30-32].

CW treatments also show good efficiency in removing micronutrients, which is highlighted by the removal of aluminum (90%) and zinc (78%) [33].

The high presence of some ions may harm plants, animals and humans, and the ammonium ion in high concentration may cause visible foliar injury. Furthermore, when the assimilation of this ion by plants is high, a significant increase of nitrogen in organic tissue may occur. Excessive absorption of ammonia and ammonium ions by the plant in addition to changing the biomass growth also modifies the sensitivity to drought and frost resistance [34]. Additionally, high concentrations of ammonium ion in water bodies can be toxic to aquatic organisms and ultimately to humans when converted to nitrate [35].

Contamination with high concentrations of chloride ions in water can damage metal pipes and concrete structures [36].

In domestic wastewater, it is common to find high concentrations of chloride and sodium because of the human diet and the composition of cleaning products such as soap. The chloride tends to remain constant through traditional processing of effluents; however, it is known that it may be decreased by ion exchange and reverse osmosis. Water containing residual chlorine with concentrations greater than 10 mg L$^{-1}$ can harm agricultural crops [30] in the same way as the reuse of water with high concentrations of sodium may cause handling problems in crops [37]. Additionally, studies show that sodium has harmful effects on soil, resulting in toxic effects for the plants [38, 39].

The alarming toxicity caused by lithium is equivalent to uranium and selenium in the early life stages of some fishes [40]. Lithium in wastewater is linked to the chemical composition of antidepressant drugs ingested by the population [41]. This type of medicine has been increasingly used in the Rio Pardo Valley region due to chronic exposure to pesticides that can increase cases of neurobehavioral disorders such as anxiety and depression [42].

On the other hand, it is possible to incorporate water from the reuse system with rainwater for use in residences and buildings. Rainwater is less polluted, and it is usually available in quantities sufficient for the processes of filtration, sedimentation and disinfection for an efficient treatment [5]. Rainwater is generally used for non-potable purposes such as for laundry, washing cars or gardening, though treated rainwater can be used for more noble purposes, even for drinking [9]. Incorporating the collected rainwater into reusable water from sludge allows for the optimization of the system and production of sufficient water quantities for building use [5].
Therefore, this study monitored cations \([\text{Na}^{+}, \text{K}^{+}, \text{Li}^{+}, \text{NH}_{4}^{+}]\) and anions \([\text{SO}_{4}^{2-}, \text{NO}_{3}^{-}, \text{NO}_{2}^{-}, \text{Cl}^{-}, \text{PO}_{4}^{3-}]\) in a constructed wetland system (CWs) for a catchment system, in sewage treatment, and in the final reusable water, as well as evaluated rainwater as a water resource in the system. The studied treatment will contribute to water reuse for small farmers in the Brazilian countryside, mainly for non-potable applications such as toilet flushing with greywater recycled. It is highlighted that monitoring ions is a helpful tool to determine the efficiency of wastewater treatment for small farms. In this way, it is also assessed if these ions are increasing after water treatment and in the reuse water.

2. Material and Methods

2.1. Rainwater capture and wastewater treatment pilot project

The project was established on a small farm in the Vera Cruz town, Rio Grande do Sul, Brazil. The aim is the treatment of two categories of water: rainwater, wastewater (from washing clothes, showers, the bathroom sink and flushing the toilet). Each type of water receives a special treatment. The sample collection points and treatment are detailed in Figure 1.

Collection of rainwater was through the house’s roof gutters. For the retention of solids, this water was driven to a 100 L tank for retention of solids, which was connected to another tank of 1000 L that was intended for the temporary storage of rainwater. Water from the temporary reservoir was disinfected, a process in which it went through two ultraviolet lamps (30 W). Rainwater after treatment was used for flushing the toilet, washing clothes and garden watering.

The wastewater from washing clothes, the shower and the bathroom sink were directed to an anaerobic filter through an independent pipeline of wastewater from toilet.

Blackwater generated exclusively from flushing the toilet was treated in the UASB reactor and subsequently in the anaerobic filter. In the anaerobic filter, gray and black water were homogenized, both being designed to remove nutrients and pathogens in a sequenced CW.
The CWs were 20 m² and were divided into four sequential tanks with 5 m² (1 m x 5 m) dimensions. The vegetation used for phytoremediation was identified as an aquatic macrophyte *Hymenachne grumosa*.

The water was stored in a 310 L tank and then pumped into a reactor for disinfection by ultraviolet radiation. After treatment the effluent was stored in a 1000 L tank for further use for flushing the toilet.

### 2.2. Ion monitoring

The samples were obtained at six different sites: municipal water (from another point in the residence), collected rainwater, into the UASB, first wetland input, last wetland output and reusable water (final of treatment). The samples were stored at 8 °C, filtered with syringe filters (0.45 µm) and analyzed for 24 h. The chromatographic analyses were performed in triplicate. The ion chromatography equipment (Model 883, Metrohn) was used with a conductivity detector. For the determination of anions, a Metrosep A Supp 5 column (150 mm x 4 mm x 5 µm) was used with a 3.2 mmol L⁻¹ sodium carbonate and 1.0 mmol L⁻¹ sodium bicarbonate solution as the mobile phase.

For the cation analysis, a Metrosep C 4 (150 mm x 4 mm x 5 µm) column was used with 1.7 mmol L⁻¹ nitric acid and 0.7 mmol L⁻¹ dipicolinic acid solutions as the mobile phase.

Ion quantification was performed by external standardization from the reference solutions with 1000 mg L⁻¹ for each ion in ultrapure water. Two curves were prepared, one for the cations (Na⁺, K⁺, Li⁺ and NH₄⁺) and the other one for the anions (SO₄²⁻, NO₃⁻, NO₂⁻, Cl⁻ and PO₄³⁻) as shown in Table 1. Detection (LOD) and quantification (LOQ) limits were determined [43].

### Table 1 Analytical curves of cations and anions

<table>
<thead>
<tr>
<th>Identification</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anions curve (mg L⁻¹)</strong></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.5</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
<td>50.0</td>
<td>100.0</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
</tr>
<tr>
<td><strong>Cations curve (mg L⁻¹)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>10.0</td>
<td>50.0</td>
<td>100.0</td>
<td>150.0</td>
<td>200.0</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
<td>15.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.5</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Samples collected at the UASB reactor could not be analyzed by ion chromatography because of high levels of organic matter. These samples were analyzed according to the methods described in Standard Methods for the Examination of Water and Wastewater [44].

Sodium and potassium ions were determined by flame photometry (B462, Micronal), sulfate ions were determined by turbidimetry (600 plus, Femto), nitrite and nitrate ions were determined by spectrophotometry in the visible region (Specord PLUS 2010, Analytik Jena) and chloride ions were determined by titrimetry.

### 2.3. Evapotranspiration

Evapotranspiration data were obtained from the Automatic Weather Station (Davis brand and Vantage Pró Plus model) at Santa Cruz do Sul University, which records the data averages every 30 min via the Weather Link 5.9 software and it is located less than 8 miles from the property where the experiment was installed.

### 3. Results and discussions

The ion chromatographic results were reliable with a good determination coefficient ($R^2$) and quantification limits (LOQ). These results were less than the values established in the 2914 ordinance of the Ministry of Health [45] which determines the allowable limits for human consumption and also less than the 357 and 430 ordinances of Ministry of Environment for discharge of final effluent. Even if water after the CWs can be reused, there is no specific ordinances stating allowable limits. That is why the comparison was made with the cited ordinances. Table 2 details the limits, values for LOD and LOQ as well as the equations of the straight line and the correlation coefficients for each ion by ion chromatography. Although the limit for sodium content is for drinking water purposes and there are no limits displayed for potassium, the monitoring of these ions helps to judge the efficiency of CWs.
Where: A = area and Q = concentration

Ordinance n. 2.914, 2011, Ministry of Health, Brazil
Ordinance n. 430, 2011, Ministry of Environment, Brazil
Ordinance n. 357, 2005, Ministry of Environment, Brazil

Tables 3 and 4 list the average results for each treatment stage after CWs is fully developed.

Water reuse results of the system evaluation period showed that the CW development was important for the effluent ion removal. Efficiency of removing potassium and ammonia reached a maximum of 99.9% for both cations, with an average efficiency of 98.4% and 99.3%, respectively.

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### Table 2
Analytical parameters of ion chromatographic analysis of Na\(^+\), K\(^+\), Li\(^+\) and NH\(_4\)\(^+\), SO\(_4^{2-}\), NO\(_3^-\), NO\(_2^-\), Cl\(^-\) and PO\(_4^{3-}\) and maximum permissible concentration of these ions in water for human consumption or in effluent emission in superficial water (vazão < 100 m\(^3\) day\(^{-1}\))

<table>
<thead>
<tr>
<th>Identification</th>
<th>P1 (mg L(^{-1}))</th>
<th>P2 (mg L(^{-1}))</th>
<th>P3 (mg L(^{-1}))</th>
<th>P4 (mg L(^{-1}))</th>
<th>P5 (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_4^{2-})</td>
<td>0.5</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>NO(_2^-)</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
<td>50.0</td>
<td>100.0</td>
</tr>
<tr>
<td>PO(_4^{3-})</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

**Cations curve (mg L\(^{-1}\))**

<table>
<thead>
<tr>
<th>Cations</th>
<th>P1 (mg L(^{-1}))</th>
<th>P2 (mg L(^{-1}))</th>
<th>P3 (mg L(^{-1}))</th>
<th>P4 (mg L(^{-1}))</th>
<th>P5 (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>10.0</td>
<td>50.0</td>
<td>100.0</td>
<td>150.0</td>
<td>200.0</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
<td>15.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>NH(_4)(^+)</td>
<td>0.5</td>
<td>1.0</td>
<td>5.0</td>
<td>10.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Where: A = area and Q = concentration

* Ordinance n. 2.914, 2011, Ministry of Health, Brazil
* Ordinance n. 430, 2011, Ministry of Environment, Brazil
* Ordinance n. 357, 2005, Ministry of Environment, Brazil

Sodium ions increased after the CWs. This behavior was also observed for the UASB/CWs system applying Hymenachne grumosa from 63.0 to 81.9 mg L\(^{-1}\) of sodium ion. The increased sodium concentration may be linked to a lower efficiency of the root system ion exchange and, more markedly, evapotranspiration. If the concentration of sodium increases, it can be removed using other process, as applied with industrial wastewater [46] or diluted with rain water according to the observations made in the experiments. In rainy seasons, this problem was minimized.

Potassium removal was effective in CWs, as shown in Table 3. The potassium ion is a macronutrient essential for plant growth [47]. The results were consistent with those obtained by removing ammonia in graywater employing zeolite (aluminosilicate tetrahedral) with negative charge on the framework [48]. Moreover, if the system is used with plants of high nutrient absorption, the removal of ammonia, phosphate and nitrates could be major [49].

Such as the cations, anions were also removed by CW treatment [Table 4]. Comparing the results from initial effluent and final reusable water, phosphate was reduced up to 96.3%. The main mechanisms of phosphorus removal by CWs system are adsorption, complexation, precipitation, absorption and assimilation by the plant [50].
system with UASB, CWs and rainwater input was efficient and suitable for small farms.

5. Acknowledgements

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6. References


