agronomy

Article

Swine Wastewater Treatment System Using Constructed Wetlands Connected in Series

Amalia García-Valero [1], José Alberto Acosta [1], Ángel Faz [1], María Dolores Gómez-López [1,*], Dora María Carmona [2], Martire Angélica Terrero [1], Oumaima El Bied [1] and Silvia Martínez-Martínez [1]

[1] Área de Ingeniería Agroforestal (Departamento de Ingeniería Agronómica), Universidad Politécnica de Cartagena, Paseo Alfonso XIII, 48, 30203 Cartagena, Murcia, Spain; angelica.terrero@upct.es (M.A.T.)
[2] Facultad de Ingeniería Química, Universidad Pontificia Bolivariana, Circular 1 No. 70-01, Medellín 050031, Colombia; dora.carmona@upb.edu.co
* Correspondence: lola.gomez@upct.es

Abstract: The main objective of this study was to analyze the efficiency of CWs for purifying swine wastewater in order to reduce its pollutant load. The system included a pretreatment module (raw swine wastewater tank, phase separator, and settlement tank), and three constructed wetlands connected in series and planted with *Phragmites australis* and *Suaeda vera*. Three treatment cycles were carried out with a total hydraulic retention time in the wetland of 21 days for each cycle. Pig slurry samples were collected in triplicate after each treatment module, and physical–chemical analyses were performed. The results showed that the phase separator decreased the suspended solids, turbidity, and the chemical oxygen demand in the treated swine wastewater. The system enabled considerable nitrogen reductions (Kjeldahl nitrogen, NH_4^+, and organic nitrogen), and the highest removal was reported in the wetlands. However, the cations and anions showed different efficiencies. In some cases (Ca, Mg, and Na), the final concentrations were increased, which could be explained by their release from the substrate; however, there were no statistical differences among the CW effluents and the raw pig slurry. Therefore, the integral pig slurry treatment system with constructed wetlands increased the quality of the treated swine wastewater and thus can be used for its sustainable agronomic valorization. This thereby enables savings in inorganic fertilizers and irrigation water.

Keywords: pig slurry; purification; pollution; nitrates

check for updates

Citation: García-Valero, A.; Acosta, J.A.; Faz, Á.; Gómez-López, M.D.; Carmona, D.M.; Terrero, M.A.; El Bied, O.; Martínez-Martínez, S. Swine Wastewater Treatment System Using Constructed Wetlands Connected in Series. *Agronomy* **2024**, *14*, 143. https://doi.org/10.3390/agronomy14010143

Academic Editor: José L. S. Pereira

Received: 26 November 2023
Revised: 3 January 2024
Accepted: 5 January 2024
Published: 7 January 2024

1. Introduction

The EU's 28 member countries are the world's second largest producers of pork, after China. Spain is the fourth largest producer (after China, the USA, and Germany), while at the European level, Spain is the second largest producer with 19% of the total tons produced [1]. Pig slurry production in the EU-28 amounts to 171.2 Mt yr^{-1}. Germany, Spain, and France are the largest producers of swine wastewater, accounting for more than 19%, 18%, and 9%, respectively [2].

Large-scale intensive pig farms generate a large amount of slurry that is difficult to manage. Consequently, pig slurry treatment from these farms is a problem that needs to be addressed due to the high levels of organic and inorganic contaminants present in the slurry and the limited availability of nearby farmland [3]. This leads to a surplus of manure in agricultural areas, which has led to the degradation of the quality of water resources.

The use of pig manure as a biofertilizer is interesting both from an ecological and an economic point of view due to its high concentrations in nitrogen, phosphorus, and potassium, amongst other nutrients. However, the intensification of pig production is considered an activity of risk to the environment when the slurry generated is not properly treated [4]. Pig farming has increasingly focused on sustainable issues and has shown significant advances in environmental management through technological development and increased awareness, especially regarding waste management [5]. This situation has led to the development of new technologies to treat this pig slurry in order to stabilize the organic matter and to concentrate and/or eliminate nutrients [6]. The selection of the most appropriate technology in each specific case depends on numerous factors, including the scale of the treatment; farm size; the need for the removal of organic matter and nutrients; cropland availability; energy generation at the facility; and the maintenance costs of the treatment plant.

Constructed wetlands (CWs) are an economical, efficient, and sustainable wastewater treatment method [7]. The technology used in CWs is considered to be a secondary or even tertiary treatment [8] that is used worldwide for treating wastewater from different sources, such as domestic, agricultural, industrial, mining, and aquifers, due to its ability to reduce pollutants in wastewater and purify it [9]. It is an environmentally sustainable alternative to existing energy intensive mechanical treatment systems, resulting in considerably lower operating costs and a reduced carbon footprint [10]. The structure of CWs is designed to simulate the physical, chemical, and biological processes occurring in natural wetlands, treating wastewater efficiently [11]. Plants and substrate are the elements that exert the greatest influence on the efficiency of the system [12,13]. Plant roots extend in the gaps of the substrate, absorb nutrients (e.g., nitrogen and phosphorus) from pore wastewater in CWs to support plant growth, and purify the water simultaneously. It should be noted that the selection of plant species is a key factor; the vegetation must survive the possible toxic effects of wastewater and its chemical variability, and, of course, must adapt to local climatic conditions. Substrates used to build wetlands include soil, sand, gravel, rock, and organic materials such as compost, which can also adsorb inorganic ions from water, especially phosphorus ions [14]. Another aspect to consider is the form of construction of the wetlands. In most cases, wetlands are built in parallel, where the pig slurry is treated in a single cell with different hydraulic retention times [15]. However, wetlands can also be built in series, where several cells are connected to each other, and pig slurry is treated in each of them continuously [16]. This way of constructing wetlands has been scarcely studied, and the efficiency of this type of construction is not known with certainty. Therefore, the objective of this study was to analyze the behavior of the physical–chemical characteristics of swine wastewater during its treatment in CWs working in series and to determine its efficiency for purifying swine wastewater in order to reduce its pollutant load for agronomic use.

2. Materials and Methods

2.1. Study Area

The study area was located in an intensive pig farm in the municipality of Torres de Cotillas (Region of Murcia, SE Spain) under a Mediterranean climate, coordinates $38^{\circ}00'51.0''$ N and $1^{\circ}15'45.2''$ W. The average temperature and precipitation during the experiment period (January to March) were 12.4 °C and 112 mm, respectively. The mean evapotranspiration was 202 mm [17]. The farm where the swine wastewater came from had 300 head of Duroc-Jersey breed mother pigs with piglets, with an average weight of 300 kg.

2.2. Treatment System and Sampling

The treatment system consisted of a pre-treatment module and a purification module, which was the constructed wetland (CW). The pre-treatment unit was equipped with a storage tank and a phase separator consisting of a press screw separator with a capacity of 5 m^3 h^{-1} equipped with a bioaeration system supplying air through a compressor of 30 m^3 h^{-1} and a sludge thickener. The solid and liquid fractions were separated with this module, and consequently the liquid fraction was treated in the CW. The purification module consisted of a CW composed of three horizontal subsurface flow cells connected in series and filled with a layer of coarse gravel and a surface layer of sand. Each wetland cell was 27 m long and 2.5 m wide, with a depth of 80 cm (60 cm of coarse gravel and 20 cm of washed sand) (Figure 1). The roughing gabion was placed in the first and last meters of the 27 m length and was filled with 4 and 8 mm diameter gravel. In addition, a polyculture was planted, using *Phragmites australis* (50%) and *Suaeda vera* (50%), with a planting density of 10 plants m^{-2} in each cell. These species were chosen because *P. australis* is the most commonly used macrophyte in wetland treatments [18], whilst *S. vera* is a halophyte that promotes the removal of soluble salts from swine wastewater. The system worked in series, i.e., the slurry passed through cell 1, then through cell 2, and finally through cell 3, remaining in each of them for a total of seven days. Three treatment cycles were carried out with a total hydraulic retention time in the wetland of 21 days for each cycle. Throughout the slurry treatment process with this system, approximately 12 m^3 could be treated in each cycle, and therefore 36 m^3 was purified. The sampling points are shown in Figure 1.

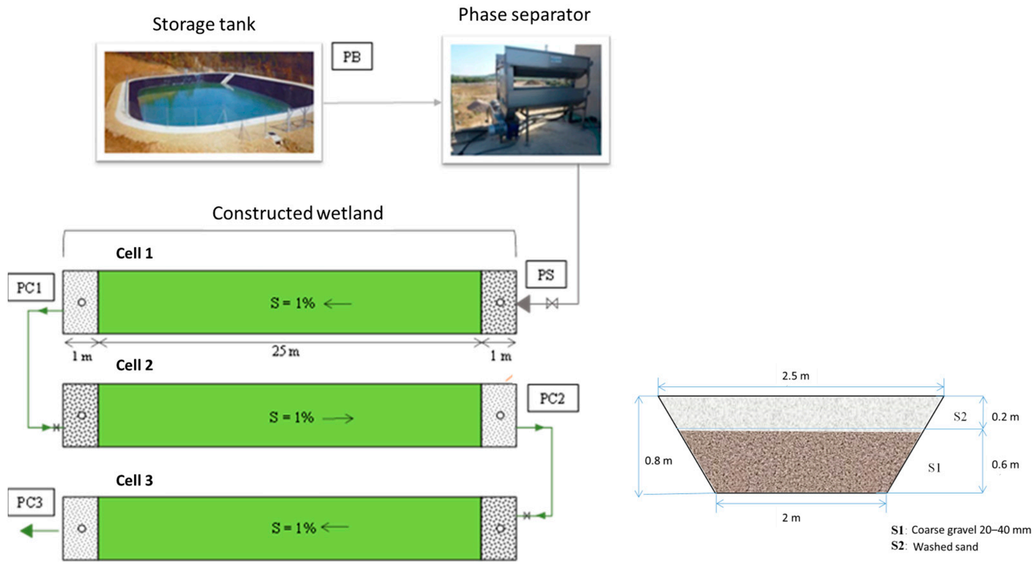

Figure 1. Swine wastewater treatment system, dimensions of each CW cell, and sampling points. PB: sampling point in the raw slurry storage tank; PS: sampling point after phase separator; PC1: sampling point at the outlet of cell 1; PC2: sampling point at the outlet of cell 2; PC3: sampling point at the outlet of cell 3; S: slope.

For each cycle, 3 samples were collected from the storage tank (PB), and another 3 samples after the phase separator (PS). After the pig slurry was in cell 1 for 7 days, 3 samples were collected (PC1). Subsequently, pig slurry remained for another 7 days in cell 2, and, after this period, 3 samples were collected (PC2). Finally, pig slurry remained for another 7 days in cell 3, and, after this period, 3 samples were collected (PC3). The samples after phase separator (PS) and from the cells (PC1, PC2, and PC3) were collected with a separation between them of 30 min. Therefore, a total of 45 samples were collected over 21 days, considering the five sampling points selected (PB, PS, PC1, PC2, and PC3), the three replicates collected per sampling point, and the three treatment cycles carried out. All samples were taken in sterile containers of 250 mL at the five sampling points.

2.3. Analytical Methods

Temperature and pH were determined in situ by a portable probe (Hanna model HI 9025, Barcelona, Spain). The electrical conductivity (EC) was analyzed in situ using a portable conductivity meter (Hanna model HI 9033, Barcelona, Spain). Kjeldahl nitrogen (KN) was analyzed using a modified Kjeldahl method [19], and using 1 mL of swine wastewater in the digestion. Ammonium nitrogen (NH_4^+-N) was determined by steam distillation and titration with HCl 0.1 N. Total nitrogen (TN) includes organic and inorganic nitrogen forms (Kjeldahl nitrogen plus nitrite and nitrate forms). Total phosphorus (TP) was photometrically determined (Macherey-Nagel GmbH & Co. KG, Düren, Germany).

Nanocolor Test; ref. 985-055). Total suspended solids (TSSs) were determined via the 2440-D method (APHA-AWWAWEF 2022). Chemical oxygen demand (COD) was determined via photometric determination (Macherey-Nagel GmbH & Co. KG, Düren, Germany. Nanocolor Test, Ref 985 028/29), (DIN 38 409-H41-1, DIN ISO 15 705-H45). Anions (Cl^-, SO_4^{2-}, NO_3^-, PO_4^{2-} and NO_2^-) were analyzed using high-performance ion chromatography (IC) (Methrom, Herisau, Switzerland, model 861), and cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and metals (Fe, Mn, Cu and Zn) were determined using an atomic absorption spectrometer (Perkin Elmer AA-Analyst 800, Waltham, MA, USA).

2.4. Statistical Analysis

To study the normality of the data distribution, the Kolmogorov–Smirnov Test was used, and transformations into logarithm were carried out to achieve normality. The homogeneity of the variance was confirmed by Bartlett's Test. One-way ANOVA was performed via a post hoc Tukey's test at $\alpha = 0.05$, which was completed to identify significant differences in the physical–chemical characteristics of treated wastewater at the sampling points (PB, PS, PC1, PC2, and PC3). Relationships between the physical–chemical characteristics of treated wastewater were studied using Pearson's correlation. Principal component analysis was used to understand the correlations among the physical–chemical characteristics of treated swine wastewater by grouping the variable into a few factors. Statistical analyses were performed using SPSS (SPSS Version 23.0, Chicago, IL, USA).

3. Results and Discussion

3.1. Characterization of Pig Slurry during the Treatment

Table 1 shows the characterization of slurry at each stage of the treatment system. As can be seen, after the phase separator, the temperature showed no significant differences with respect to the raw slurry, with a value of 12.9 ± 1.6 °C in the storage tank. In the wetland, a higher temperature, between one and three degrees Celsius, was observed than in the previous stages (PB and PS). According to certain authors [4,8], constructed wetlands can maintain a higher temperature due to substrate and plant roots, which likely benefits microbial activity within the CW. In addition, CWs are characterized by having buffering functions, referring to the temperature within the wetland in relation to the ambient temperature [4]. In addition, seasonal temperatures can produce changes in the activation of microorganisms, with pathogens being better eliminated at high temperatures [20].

The swine wastewater pH had a slight non-significant increase after the phase separator (Table 1). The mean pH values were slightly alkaline, showing almost identical values of around eight at the end of the CWs; oppositely, Schierano et al. [21] found a reduction in pH values (from 8.55–9.25 to 7.95–8.75) after CWs. Generally, electrical conductivity (EC) tends to be high in pig slurry due to the salt-based and high-protein diets needed to meet the needs of pigs [22]. The EC in the PS was significantly lower with respect to raw slurry. Andreo-Martínez [23] indicated that the physical separation of the solid and liquid fraction of pig slurry could reduce EC due to the chemical precipitation of salts in the solid phase. In addition, the EC showed a trend to decrease in the CWs, decreasing successively in PC1, PC2, and PC3. However, the observed decrease was only significant for PC3, which could be due to a release of ions from the CWs caused by the interaction between the substrate and the biofilm within the wetland [4]. The anions showed no significant differences between the PB and the resulting slurry in PC3, except for PO_4^{3-}, NO_3^-, and SO_4^{2-}, which decreased from 147 ± 39.7 mg L^{-1} to 35.4 ± 4.3 mg L^{-1} for PO_4^{3-}, whilst increasing significantly for SO_4^{2-} and NO_3^- (Table 1). The cations also showed no statistically significant differences, except for K+, with concentrations of 787 ± 25.9 mg L^{-1} for raw slurry and 312 ± 22.3 mg L^{-1} for slurry after passing through the CWs.

Table 1. Physical–chemical characterization of pig slurry at each stage of the treatment system.

	PB	PS	PC1	PC2	PC3
T (°C)	12.9 ± 1.6	13.5 ± 2.5	14.3 ± 2.7	14.7 ± 1.5	17.6 ± 2.9
pH	7.8 ± 0.1	8.2 ± 0.2	8.1 ± 0.4	8.1 ± 0.3	7.9 ± 0.2
EC (dS m^{-1})	13.5 ± 0.4 a	10.1 ± 1.7 b	10.8 ± 1.3 b	10.6 ± 1.6 b	7.6 ± 1.3 c
SS (g L^{-1})	158 ± 25.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
TSS (g L^{-1})	13.2 ± 2.4	10.1 ± 1.3	8.7 ± 2.0	9.0 ± 0.5	10.6 ± 2.9
Turbidity (NTU)	213 ± 39 a	52 ± 8 b	86 ± 29 b	69 ± 16 b	76 ± 13 b
COD (g L^{-1})	4.3 ± 1.8 a	0.8 ± 0.6 b	0.9 ± 0.5 b	1.0 ± 0.4 b	0.8 ± 0.3 b
KN (g L^{-1})	1.5 ± 0.1 a	0.7 ± 0.1 b	0.9 ± 0.3 b	0.8 ± 0.2 b	0.2 ± 0.1 c
N-NH_4^+ (g L^{-1})	0.9 ± 0.1 a	0.4 ± 0.1 b	0.5 ± 0.2 ab	0.5 ± 0.2 ab	0.1 ± 0.0 c
ON (g L^{-1})	0.4 ± 0.2 a	0.2 ± 0.0 b	0.2 ± 0.0 b	0.2 ± 0.1 b	0.1 ± 0.1 b
TN (g L^{-1})	1.6 ± 0.1 a	0.9 ± 0.2 b	1.1 ± 0.4 ab	1.0 ± 0.2 b	0.5 ± 0.0 c
Cl^- (mg L^{-1})	762 ± 55	915 ± 213	733 ± 102	769 ± 16	1011 ± 81
N-NO_2^- (mg L^{-1})	0.0 ± 0.0	69.7 ± 44.4	62.7 ± 6.9	6.9 ± 1.9	1.6 ± 0.8
N-NO_3^- (mg L^{-1})	7.5 ± 1.2 b	9.6 ± 3.8 b	5.4 ± 1.8 b	5.1 ± 1.4 b	100.3 ± 28.2 a
PO_4^{3-} (mg L^{-1})	147 ± 39 a	50 ± 13 b	41 ± 15 b	37 ± 16 b	35 ± 4 b
SO_4^{2-} (mg L^{-1})	152 ± 51 b	1515 ± 591 a	838 ± 161 a	544 ± 53 a	1514 ± 496 a
Na^+ (mg L^{-1})	425 ± 2	604 ± 172	462 ± 65	484 ± 17	1107 ± 366
K^+ (mg L^{-1})	787 ± 25 a	376 ± 18 b	513 ± 35 ab	402 ± 70 b	312 ± 22 b
Ca^{+2} (mg L^{-1})	322 ± 131	298 ± 169	171 ± 70	207 ± 67	416 ± 137
Mg^{+2} (mg L^{-1})	97 ± 9	219 ± 95	150 ± 25	148 ± 6	252 ± 114
Cu (mg L^{-1})	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
Zn (mg L^{-1})	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
Fe (mg L^{-1})	0.8 ± 0.2	1.0 ± 1.3	1.1 ± 0.5	1.0 ± 0.4	0.4 ± 0.3
Mn (mg L^{-1})	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.1

Mean ± standard deviation. Data expressed on a fresh-weight basis. Rows with different letters indicate significant differences at $p < 0.05$. PB: raw pig slurry; PS: slurry after phase separator; PC1: slurry after cell 1 of the wetland; PC2: slurry after cell 2 of the wetland; PC3: slurry after cell 3 of the wetland; T: temperature; EC: electrical conductivity; SSs: settleable solids; TSSs: total suspended solids; COD: Chemical Oxygen Demand; KN: Kjeldahl nitrogen; N-NH_4^+: nitrogen as ammonia; ON: organic nitrogen; TN: total nitrogen; Cl^-: chloride; N-NO_2^-: nitrogen as nitrites; N-NO_3^-: nitrogen as nitrates; PO_4^{3-}: phosphate; SO_4^{2-}: sulphate; Na^+: sodium; K^+, potassium; Ca^{2+}: calcium; Mg^{2+}: magnesium; Cu: copper; Zn: Zinc; Fe: iron; and Mn: manganese.

The TSSs showed no significant differences between PB and PS. The mean TSS values in PC1, PC2, and PC3 were slightly lower compared to the results obtained for PB but without reaching statistical significance; therefore, the system does not remove TSSs from the wastewater. The main process involved in this removal could be explained by the sedimentation of particles during the treatment [24,25] and likely a longer hydraulic retention time will be necessary to remove TSSs [26]. In this study, TSSs were completely eliminated after the phase separator. Therefore, it was not possible to evaluate the effect of the CWs on the reduction in this parameter. However, other studies found high reductions in suspended solids when the wastewater was treated in constructed wetlands, with reductions of 83 and 95% [27,28].

Chemical oxygen demand (COD) showed statistically significant differences between PB and PS. However, no statistically significant differences were found between the wetland cells, highlighting the removal of organic compounds in the phase separator [4]. The main mechanisms for organic matter elimination in CWs are filtration and sedimentation on a substrate, and, on the other hand, microbiological degradation on the root system. However, due to the low input values of COD to the wetlands in this study (0.8–1 mg L^{-1}), these effects could not be observed.

For nitrogen, in all its forms, statistically significant differences were found in the slurry after treatment. In the case of TN, treatment in the constructed wetland in series was efficient; it decreased progressively in the three cells, with mean values in PC1 of 1.1 ± 0.4 g L^{-1}, PC2 of 1.0 ± 0.2 g L^{-1}, and PC3 of 0.6 ± 0.0 g L^{-1}. In addition, the concentrations of ON, KN, and N-NH_4^+ were also decreased in the CWs, from 0.2, 0.7, and 0.4 g L^{-1} to 0.1, 0.2, and 0.1 g L^{-1}, respectively. The main mechanisms for nitrogen removal are nitrification, denitrification, adsorption, and absorption [8]. Ion exchange can significantly affect the adsorption of N-NH_4^+ [25]. The main mechanism of N-NH_4^+ removal in CWs is ion exchange adsorption on substrates, which is a reversible process based on the adsorption capacity of substrate materials [29].

Finally, metals (Cu, Zn, Fe, and Mn) showed no statistically significant differences in the different stages of the treatment. Koretsky et al. [30] observed that the pH of the sediments that make up the system was responsible for the mobility reduction in metals in wetlands. However, Vymazal et al. [31] found that an alkaline pH in wetland-treated wastewater, such as that found in this study, had no influence, so it did not affect the mobility and retention of the metals. Moreover, another study found a correlation between TSS and metal removal [32], which would explain that the metals removed by CWs were due to bound solids that were settled.

3.2. Efficiency of the Treatment System

The efficiency was calculated after the phase separator (effect of the phase separator compared to the raw pig slurry), after the CW (effect of CWs compared to the phase separator), and the total efficiency of the treatment system (effect of CWs compared to the raw pig slurry). It should be noted that the minus sign means that the parameter increased with respect to the initial value (Table 2).

Table 2. Treatment system purification efficiencies (%).

	Phase Separator	Constructed Wetland	Total Efficiency
EC	25	25	44
SS	100		100
TSS	23	−5	20
Turbidity	75	−47	64
COD	81	0	81
KN	53	71	87
NH_4^+	58	80	92
ON	50	51	75
TN	44	33	63
Cl^-	−20	−10	−33
PO_4^{3-}	65	30	76
Na^+	−42	−83	−160
K^+	52	17	60
Ca^{2+}	7	−40	−29
Mg^{2+}	−124	−15	−158
Fe	−25	60	50

Determination of the treatment system purification efficiencies (%). EC: electrical conductivity; SSs: settleable solids; TSSs: total suspended solids; COD: Chemical Oxygen Demand; NK: Kjeldahl nitrogen; NH_4^+: ammonia nitrogen; ON: organic nitrogen; TN: total nitrogen; Cl^-: chloride; NO_2^-: nitrites; PO_4^{3-}: phosphate; SO_4^{2-}: sulphate; Na^+: sodium; K^+: potassium; Ca^{2+}: calcium; Mg^{2+}: magnesium; Cu: copper; Zn: Zinc; Fe: iron; and Mn: manganese.

The pH varied from 7.8 in the influent to 7.8 in the effluent of the CW (Table 1), without a statistical difference. In the case of the EC, the phase separator decreased its value by 25%, whilst the wetland also enabled us to reduce the EC by 25%, with a total reduction of 44%. In other studies, in which pig slurry was treated in a CW composed of one cell, lower efficiencies were obtained, around 7.8 and 5.6% for 7 days and 3 days of hydraulic retention time, respectively [4,8]. In this study, the efficiency of the phase separator was high, possibly due to the precipitation of salts in the solid fraction, which would enable us to reduce the concentration of salts, and, therefore, the EC of the liquid fraction. Similarly, the reduction in salinity was high in the wetland, possibly due both to the absorption of nutrients by *Phragmites* and *Sudaea* and to the precipitation of salts on the substrate and adsorption in settleable fine particles.

The overall efficiency for SS, STS, and turbidity was high, especially for SS and turbidity, whose efficiencies reached 100% and 64%, respectively. However, the wetland caused the values for these parameters to increase, having negative efficiencies. The results showed that the TSSs were reduced by 23% using mechanical separation. Previous studies indicated that a mechanical pre-treatment prior to the use of CWs prevents the obstruction of the CWs and extends the useful life of the system [33]. The COD had a total efficiency of 81%, which was obtained after the pig slurry was treated with the phase separator. However, in other studies where CWs were used, efficiencies of 33% were obtained in unplanted cells or even 56–60% in planted cells [4].

Nitrogen in the forms of KN, NH_4^+, and ON had a total efficiency between 75 and 90%, with the wetland providing the highest efficiency in the system. Zhang et al. [34] recorded 40–50% KN removal. Nitrification and denitrification processes could influence the variations in KN and NH_4^+ in the CWs. Oxygen from the atmosphere together with the release of oxygen from the rhizosphere would favor nitrification processes, whilst anaerobic conditions in the lower part of the CWs would favor denitrification [35]. The behavior of the anions was very heterogeneous, with extremely high values being obtained, especially in the cases of N-NO_2^-, N-NO_3^-, and SO_4^{2-}, with a total increase in the N-NO_2^-, N-NO_3^-, and SO_4^2 concentrations from 0.03 to 1.6 mg L^{-1}, from 7,5 to 100 mg L^{-1}, and from 152 to 1514 mg L^{-1}, respectively (Table 1). The cations increased as they passed through the system, showing negative total efficiencies, except for K^+ with a total efficiency of 60%; this was due to the release of cations, especially of calcium and magnesium, from the calcareous substrate used in constructing the wetland.

Finally, only Fe had a positive efficiency, mainly due to the passage of this metal through the wetland. Similar research indicated that more than 50% of heavy metals can be adsorbed to wetland particles and could be removed by sedimentation [8], with efficiencies being found of under 5% for Cu [36] and of 8 and 27% for Zn and Mn, respectively [4].

3.3. Relationship between Physical–Chemical Properties of Swine Wastewater in the Treatment System

Table 3 presents the correlation matrix between the physical–chemical properties of the swine wastewater in the treatment system. As can be seen, EC had a high correlation with settleable solids (SSs), TSSs, and turbidity, indicating that the salts would be precipitating on the settleable particles of the pig slurry, which would decrease the turbidity and EC of the treated swine wastewater in the wetlands [37]. Similarly, there was a high correlation between SS, TSS, and turbidity, since the filtration process that takes place both in the phase separator and in the constructed wetland decreases the SS and TSS concentrations, and consequently the turbidity [38]. COD is also positively correlated with the abovementioned parameters; this is due to the effect of both the phase separator and the wetland substrate. The phase separator allows the separation of the solid phase of the slurry, thus reducing the organic matter present in the liquid fraction [8]. Just as CW can intercept insoluble organic contaminants by mechanical retention in the substrate such as filtration, precipitation, and adsorption, bacteria and plants can also absorb dissolved organic contaminants [37].

Table 3. Pearson correlation coefficients of parameters in the treatment system.

	T	pH	EC	SS	STS	Turb	COD	KN	NH_4^+	ON	TN	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cu	Zn	Fe
pH	−0.72	1																					
EC	−0.33	−0.14	1																				
SS	−0.08	−0.37	0.96	1																			
STS	0.18	−0.41	0.77	0.89	1																		
Turbidity	0.12	−0.56	0.85	0.96	0.94	1																	
COD	−0.1	−0.38	0.96	0.99	0.87	0.95	1																
KN	−0.35	−0.2	0.98	0.93	0.68	0.81	0.94	1															
NH_4	−0.44	−0.12	0.97	0.89	0.62	0.76	0.91	0.99	1														
ON	−0.08	−0.42	0.95	0.97	0.8	0.91	0.98	0.96	0.92	1													
TN	−0.14	−0.31	0.97	0.96	0.77	0.86	0.97	0.96	0.94	0.98	1												
Cl^-	0.9	−0.45	−0.53	−0.29	0.1	−0.06	−0.32	−0.59	−0.67	−0.36	−0.41	1											
NO_2^-	−0.58	0.9	−0.28	−0.52	−0.65	−0.73	−0.51	−0.28	−0.2	−0.48	−0.36	−0.44	1										
NO_3^-	0.96	−0.55	−0.49	−0.24	0.1	−0.02	−0.27	−0.54	−0.62	−0.28	−0.34	0.98	−0.48	1									
PO_4^{3-}	0.48	−0.54	0.59	0.76	0.94	0.85	0.74	0.49	0.42	0.68	0.65	0.36	−0.7	0.38	1								
SO_4^{2-}	0.43	0.19	−0.88	−0.79	0.44	−0.65	−0.81	−0.95	−0.96	−0.87	−0.88	0.73	0.16	0.64	−0.25	1							
Na^+	0.86	−0.36	−0.6	−0.38	0.01	−0.16	−0.41	−0.67	−0.74	−0.45	−0.5	0.99	−0.35	0.96	0.28	0.8	1						
K^+	−0.31	−0.19	0.98	0.92	0.66	0.79	0.93	0.99	0.98	0.96	0.98	−0.58	−0.24	−0.52	0.5	−0.95	−0.66	1					
Ca^{2+}	0.76	−0.43	−0.21	0.03	0.45	0.26	−0.01	−0.32	−0.4	−0.09	−0.16	0.9	−0.59	0.85	0.63	0.55	0.88	−0.33	1				
Mg^{2+}	0.54	0.09	−0.79	−0.66	−0.26	−0.5	−0.69	−0.88	−0.9	−0.76	−0.77	0.82	0.04	0.74	−0.06	0.98	0.88	−0.87	0.69	1			
Cu	−0.46	0.62	−0.02	−0.26	−0.51	−0.5	−0.24	0.01	0.06	−0.14	−0.02	−0.53	0.87	−0.5	−0.52	−0.16	−0.49	0.08	−0.73	−0.26	1		
Zn	−0.65	0.71	0.19	−0.07	−0.34	−0.34	−0.05	0.2	0.26	0.01	0.14	−0.69	0.85	−0.68	−0.44	−0.32	−0.65	0.26	−0.77	−0.4	0.95	1	
Fe	−0.9	0.72	0.16	−0.12	−0.45	−0.36	−0.09	0.21	0.3	−0.04	0.04	−0.89	0.78	−0.9	−0.66	−0.38	−0.84	0.22	−0.93	−0.52	0.77	0.86	1
Mn	0.72	−0.13	−0.63	−0.44	−0.01	−0.25	−0.48	−0.73	−0.78	−0.55	−0.57	0.94	−0.19	0.88	0.22	0.88	0.97	−0.72	0.86	0.95	−0.41	−0.55	−0.74

T: temperature; EC: electrical conductivity; SSs: settleable solids; TSSs: total suspended solids; COD: Chemical Oxygen Demand; NK: Kjeldahl nitrogen; NH4+: ammonia nitrogen; ON: organic nitrogen; TN: total nitrogen; Cl^-: chloride; NO_2^-: nitrites; PO_4^{3-}: phosphate; SO_4^{2-}: sulphate; Na^+: sodium; K^+: potassium; Ca^{2+}: calcium; Mg^{2+}: magnesium; Cu: copper; Zn: Zinc; Fe: iron and Mn: manganese. Statistically significant relationships at the 95% confidence level (red color).

All forms of nitrogen correlated positively with each other (Table 3). KN in most livestock wastewater is found in inorganic forms, mainly as ammonium, and therefore could be adsorbed by colloids of suspended organic matter [39]. At the same time, the reduction in TN could be due to the nitrification–denitrification process that occurs in the CW [4].

Anions and cations have a very heterogeneous correlation; in many cases, it was positive due to the absorption and adsorption action of the wetland, and in others it was negative due to their release by the substrate [40].

The results of the principal component analysis indicate that the variables evaluated were grouped into three components, representing 81.3% of the variability (Table 4). In the first component (C1), EC, SS, STS, COD, turbidity, KN, ON, TN, ammonium, sulphates, phosphates, and potassium were grouped, which shows that a reduction in the concentration of solids after the treatment system would lead to a significant reduction in turbidity, COD, salinity, and some anions and cations, as well as the concentrations of the different forms of nitrogen, with the exception of nitrates and nitrites. Conversely, temperature, sodium, magnesium, and manganese were grouped in C2, indicating that the variations observed in these elements during the pig slurry treatment have a common origin, either adsorption, absorption, or precipitation processes. Finally, pH, copper, zinc, iron, and calcium were grouped in C3, indicating that the pH of the treated water was the main factor that controlled the concentrations of those elements in the wastewater.

Table 4. Results of the principal component analysis.

Component	C1	C2	C3	Extraction
Temperature	0.025	0.792	0.356	0.805
pH	0.009	0.3	0.653	0.773
Electrical conductivity	0.865	0.094	0.404	0.922
Settleable solids	0.867	−0.141	−0.081	0.788
Total suspended solids	0.743	0.478	−0.366	0.932
Turbidity	0.812	−0.016	−0.214	0.736
Chemical Oxygen Demand	0.952	−0.046	−0.13	0.932
Kjeldahl nitrogen	0.928	−0.158	0.317	0.987
Ammonium	0.843	−0.188	0.477	0.974
Organic nitrogen	0.909	−0.035	−0.227	0.881
Total nitrogen	0.908	−0.028	0.32	0.931
Nitrites	−0.306	0.002	0.041	0.87
Nitrates	−0.343	0.412	−0.205	0.622
Phosphates	0.652	0.577	−0.33	0.868
Sulphates	0.654	0.565	−0.392	0.974
Sodium	−0.194	0.937	−0.248	0.979
Potassium	0.872	−0.008	0.454	0.967
Calcium	0.008	0.534	−0.819	0.958
Magnesium	−0.432	0.817	−0.262	0.97
Copper	0.02	0.061	0.696	0.776
Zinc	0.013	−0.178	0.863	0.789
Iron	0.123	−0.213	0.899	0.876
Manganese	−0.264	0.775	−0.506	0.93
% Variance	39.4	26.9	15	
% Cumulative variance	39.4	66.3	81.3	

4. Conclusions

The results showed that the phase separator enabled a considerable reduction in SS, which was reduced in its entirety at this stage, obtaining an efficiency of 100%. In addition, TSS, turbidity, and COD were also reduced when swine wastewater was treated using the mechanical separator. This system allowed considerable reductions in nitrogen (KN, NH_4^+, and ON), which were obtained mainly in the wetland cells. However, the cations and anions showed different efficiencies in the treatment system, and, in some cases, the final concentrations were even higher than the initial ones, which could be explained by their release from the substrate.

Therefore, it can be established that the integrated slurry treatment system with biofilters (constructed wetlands) is effective in reducing the concentrations of some compounds, thus contributing to a higher-quality treated pig slurry, which can be used for its sustainable agronomic valorization, and, in turn, leads to savings in inorganic fertilizers and irrigation water.

Author Contributions: Conceptualization, M.D.G.-L. and S.M.-M.; methodology, J.A.A. and S.M.-M.; software, A.G.-V., O.E.B. and M.A.T.; formal analysis, A.G.-V., O.E.B., D.M.C. and M.A.T.; investigation, A.G.-V., O.E.B. and M.A.T.; resources, Á.F.; data curation, M.D.G.-L., D.M.C. and S.M.-M.; writing—original draft preparation, A.G.-V. and J.A.A.; writing—review and editing A.G.-V., S.M.-M. and J.A.A.; supervision, J.A.A.; project administration, Á.F.; funding acquisition, Á.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available upon request to the corresponding author. The data are not publicly available due to confidentiality.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Eurostat. 2019. Available online: https://ec.europa.eu/eurostat/data/database (accessed on 15 October 2023).
2. Makara, A. Comparative analyses of pig farming management systems using the Life Cycle Assessment method. *J. Clean. Prod.* **2019**, *241*, 118305. [CrossRef]
3. Lee, Y.S.; Han, G.B. Pig slurry treatment by a hybrid multi-stage unit system consisting of an ATAD and an EGSB followed by a SBR reactor. *Biosyst. Eng.* **2012**, *111*, 243–250. [CrossRef]
4. Terrero, M.A. Efficiency of an integrated purification system for pig slurry treatment under mediterranean climate. *Agronomy* **2020**, *10*, 208. [CrossRef]
5. Secco, C. Circular economy in the pig farming chain: Proposing a model for measurement. *J. Clean. Prod.* **2020**, *260*, 121003. [CrossRef]
6. Marti, E. Pharmaceuticals removal in an on-farm pig slurry treatment plant based on solid-liquid separation and nitrification-denitrification systems. *Waste Manag.* **2020**, *102*, 412–419. [CrossRef]
7. Ji, Z.; Tang, W.; Pei, Y. Constructed wetland substrates: A review on development, function mechanisms, and application in contaminants removal. *Chemosphere* **2022**, *286*, 131564. [CrossRef]
8. Caballero-Lajarín, A. Combination of Low-Cost Technologies for Pig Slurry Purification under Semiarid Mediterranean Conditions. *Water Air Soil Pollut.* **2015**, *226*, 341. [CrossRef]
9. Gill, L.W. Long term heavy metal removal by a constructed wetland treating rainfall runoff from a motorway. *Sci. Total Environ.* **2017**, *601–602*, 32–44. [CrossRef]
10. Stefanakis, A.I. The role of constructed wetlands as green infrastructure for sustainable urban water management. *Sustainability* **2019**, *11*, 6981. [CrossRef]
11. Bakhshoodeh, R.; Alavi, N.; Paydary, P. Composting plant leachate treatment by a pilot-scale, three-stage, horizontal flow constructed wetland in central Iran. *Environ. Sci. Pollut. Res.* **2017**, *24*, 23803–23814. [CrossRef]
12. Lu, S. Impacts of different media on constructed wetlands for rural household sewage treatment. *J. Clean. Prod.* **2016**, *127*, 325–330. [CrossRef]
13. Khalifa, M.E.; El-Reash, Y.G.A.; Ahmed, M.I.; Rizk, F.W. Effect of media variation on the removal efficiency of pollutants from domestic wastewater in constructed wetland systems. *Ecol. Eng.* **2020**, *143*, 105668. [CrossRef]
14. Zhuang, L.-L.; Yang, T.; Zhang, J.; Li, X. The configuration, purification effect and mechanism of intensified constructed wetland for wastewater treatment from the aspect of nitrogen removal: A review. *Bioresour. Technol.* **2019**, *293*, 122086. [CrossRef] [PubMed]
15. Wang, Q.; Hernández-Crespo, C.; Santoni, M.; Van Hulle, S.; Rousseau, D.P.L. Horizontal subsurface flow constructed wetlands as tertiary treatment: Can they be an efficient barrier for microplastics pollution? *Sci. Total Environ.* **2020**, *721*, 137785. [CrossRef]
16. Pradeep, K.S.; Deepa, M.; Anju, R.; Piyush, M. Treatment efficiency of vertical flow constructed wetland systems operated under different recirculation rates. *Ecol. Eng.* **2018**, *120*, 474–480.
17. SIAM. Available online: http://siam.imida.es/ (accessed on 10 October 2023).
18. Barco, A.; Borin, M. Treatment performance and macrophytes growth in a restored hybrid constructed wetland for municipal wastewater treatment. *Ecol. Eng.* **2017**, *107*, 160–171. [CrossRef]
19. Duchaufour, P. *Precis de Pedologie*; Masson: Paris, France, 1970.

20. Shingare, R.P. Constructed wetland for wastewater reuse: Role and efficiency in removing enteric pathogens. *J. Environ. Manag.* **2019**, *246*, 444–461. [CrossRef]
21. Schierano, M.C.; Panigatti, M.C.; Maine, M.A.; Griffa, C.A.; Boglione, R. Horizontal subsurface flow constructed wetland for tertiary treatment of dairy wastewater: Removal efficiencies and plant uptake. *J. Environ. Manag.* **2020**, *272*, 111094. [CrossRef]
22. Hjorth, M. Solid-liquid separation of animal slurry in theory and practice. *Sustain. Agric.* **2009**, *2*, 953–986.
23. Andreo-Martínez, P. Domestic wastewaters reuse reclaimed by an improved horizontal subsurface-flow constructed wetland. *Bioresour. Technol.* **2017**, *233*, 236–246. [CrossRef]
24. El Bied, O. Purification performance of filtration process for pig slurry using marine sands, silty loam soils, fly ash and zeolite. *Agronomy* **2021**, *118*, 1608. [CrossRef]
25. Batool, A.; Saleh, T.A. Removal of toxic metals from wastewater in constructed wetlands as a green technology; catalyst role of substrates and chelators. *Ecotoxicol. Environ. Saf.* **2020**, *189*, 109924. [CrossRef] [PubMed]
26. De La Mora-Orozco, C.; González-Acuña, I.J.; Saucedo-Terán, R.A.; Flores-López, H.E.; Rubio-Arias, H.O.; Ochoa-Rivero, J.M. Removing organic matter and nutrients from pig farm wastewater with a constructed wetland system. *Int. J. Environ. Res. Public Health* **2018**, *15*, 1031. [CrossRef] [PubMed]
27. Idris, S.M.; Jones, P.L.; Salzman, S.A.; Croatto, G.; Allinson, G. Evaluation of the giant reed (*Arundo donax*) in horizontal subsurface flow wetlands for the treatment of recirculating aquaculture system effluent. *Environ. Sci. Pollut. Res.* **2012**, *19*, 1159–1170. [CrossRef] [PubMed]
28. de Queiroz, R.d.C.S.; Maranduba, H.L.; Hafner, M.B.; Rodrigues, L.B.; de Almeida Neto, J.A. Life cycle thinking applied to phytoremediation of dairy wastewater using aquatic macrophytes for treatment and biomass production. *J. Clean. Prod.* **2020**, *267*, 122006. [CrossRef]
29. Jóźwiakowski, K.; Bugajski, P.; Mucha, Z.; Wójcik, W.; Jucherski, A.; Nastawny, M.; Siwiec, T.; Mazur, A.; Obroślak, R.; Gajewska, M. Reliability and efficiency of pollution removal during long-term operation of a one-stage constructed wetland system with horizontal flow. *Separ. Purif. Technol.* **2017**, *187*, 60–66. [CrossRef]
30. Koretsky, C.M. Influence of *Spartina* and *Juncus* on Saltmarsh Sediments. I. Pore Water Geochemistry. *Chem. Geol.* **2008**, *255*, 87–99. [CrossRef]
31. Vymazal, J. Heavy metals in sediments from constructed wetlands treating municipal wastewater. *Biogeochemistry* **2010**, *101*, 335–356. [CrossRef]
32. Terzakis, S. Constructed wetlands treating highway runoff in the central Mediterranean region. *Chemosphere* **2008**, *72*, 141–149. [CrossRef]
33. Burton, C.H. The potential contribution of separation technologies to the management of livestock manure. *Livest. Sci.* **2007**, *112*, 208–216. [CrossRef]
34. Zhang, D.Q. Application of constructed wetlands for wastewater treatment in tropical and subtropical regions (2000–2013). *J. Environ. Sci.* **2015**, *30*, 30–46. [CrossRef] [PubMed]
35. Doherty, L. Nutrient and organics removal from swine slurry with simultaneous electricity generation in an alum sludge-based constructed wetland incorporating microbial fuel cell technology. *Chem. Eng. J.* **2015**, *266*, 74–81. [CrossRef]
36. Muñoz, M.A. Effects of the Hydraulic Retention Time on Pig Slurry Purification by Constructed Wetlands and Stabilization Ponds. *Water Air Soil Pollut.* **2016**, *227*, 293. [CrossRef]
37. Guo, X.; Cui, X.; Li, H. Effects of fillers combined with biosorbents on nutrient and heavy metal removal from biogas slurry in constructed wetlands. *Sci. Total Environ.* **2020**, *703*, 134788. [CrossRef]
38. Popovic, O. Improved pig slurry mechanical separation using chitosan and biochar. *Biosyst. Eng.* **2014**, *127*, 115–124. [CrossRef]
39. Borin, M.; Politeo, M.; De Stefani, G. Performance of a hybrid constructed wetland treating piggery wastewater. *Ecol. Eng.* **2013**, *51*, 229–236. [CrossRef]
40. García-Valero, A.; Martínez-Martínez, S.; Faz, A.; Terrero, M.A.; Muñoz, M.A.; Gómez-López, M.D. Treatment of Wastewater from the Tannery Industry in a Constructed Wetland Planted with *Phragmites australis*. *Agronomy* **2020**, *10*, 176. [CrossRef]