Purification Performance of Filtration Process for Pig Slurry Using Marine Sands, Silty Loam Soils, Fly Ash and Zeolite

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Received: 5 May 2021 Accepted: 5 August 2021 Published: 12 August 2021

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Abstract: Filtration is a simple ecological process for the treatment of effluents. This research examined the physicochemical properties of micronutrients, macronutrients, and heavy metals (HM) removed after the slow filtration of pig slurry (PS) through multiple media: sands, silt loam soils, fly ash, and zeolite. The objective was to find a new layer that can be added to our constructed wetland (CW) to improve its efficiency and study how the slurry reacts to these natural materials. The filtration achieved an approximate removal rate of 99.99% for total suspended solids (TSS) and nitrogen and 61, 94, 72, and 97%, respectively, for electrical conductivity (EC), turbidity, chemical oxygen demand (COD), and five-day biological oxygen demand (BOD5). The two sands, soil 1, and zeolite, had a macronutrient reduction median of 60%, whereas soil 2, 3, 4, and fly ash released macronutrients such as Na, Ca, and Mg. All the media achieved nearly 99.99% micronutrient removal for Fe and Zn. The Cu removal rate was over 86% except for sand 1 and 2 and soil 1, which reduced it to only 46%; the overall Mn removal rate was more than 80% except for soil 3 and soil 4, where it was only 9%. Zeolite had a 99.99% removal capacity for HM as opposed to sand 2, soil 4, and fly ash, which released some HMs (Ni, Cu). This inexpensive and abundant media filtration process is sound technically and financially sound and seems to be an ideal cost-efficient treatment for pig slurry.

Keywords: pig slurry; pig slurry filtration; multi-material media; heavy metals removal; physicochemical properties; cost-efficient wastewater treatment; micronutrients; macronutrients; constructed wetlands

1. Introduction

Pigs are the main category of domesticated livestock within the European Union and account for almost half of all European meat production. About half of the EU total of 150 million pigs is produced in Germany, Spain, and France. Competition has led to both structural and geographic concentrations of pig farms [1], resulting in an increasing amount of nitrogen, phosphorus, and other elements in increasing concentrations of manure that must be treated to conform to strict EU environmental legislation.

Council Directive 91/676/EEC, concerning water protection from pollution caused by agricultural nitrates, requires EU member states to identify sensitive zones where action plans must be adopted to reduce the effects of certain farm practices [2] The Murcia region on Spain’s southeast coast is one such sensitive zone. According to the national census, it is one of the most important livestock regions, contributing 1977 million heads, representing 6.32% of the national total [3]. The severe rules imposed by the European Union show how important it is to treat and manage pig slurry to limit its negative environment impact.

Pig manure affects surface and groundwater mainly because of organic and inorganic nitrogen (ammonia and nitrates) and phosphorus that runoff from ensiled effluent and...
sludge [4]. Nitrates can leach into the soil and pollute water at a depth greater than one meter from the surface [5]. Pig slurry also holds significant amounts of heavy metals, particularly Cu and Zn [4]. Heavy metals are one of the most persistent pollutants because they cause soil degradation, reduce soil buffering capacity, and permanently contaminate the soil and groundwater [6]. An important source of heavy metals is agricultural development, especially intensive pig production [4], so finding a method to treat this effluent is one of our research objectives.

Treatment plants have different methods of extracting metallic “micronutrients” from pig slurry that are then turned into fertilizer. These methods employ physicochemical, biological, or activated sludge processes. Choosing the right treatment technique depends on various factors, such as the size of the facility, its installation, and maintenance costs, required depuration level, and organic matter and nutrient removal [7]. However, one of the newest and most economical techniques is a constructed wetland (CW) [8]. Various studies [9,10] proved that it could successfully treat wastewater from agriculture, aquaculture, and industry. Angelica Terrero [5] showed that a CW reduced 85% of total suspended solids (TSS), and the total Kjeldahl removal of nitrogen and phosphorus was 33% of the manure’s chemical oxygen demand (COD). However, the CW could not reduce electrical conductivity or water hardness, two factors that can limit the reuse of treated pig slurry, especially as a fertilizer.

The vertical flow of the CW extends from the surface down through 0.30 m of washed sand, 0.10 m of fine gravel, 0.50 m of coarse gravel, and 0.30 m of fine gravel [5]. A new layer will be added in the third position from the top just after the fine gravel. This work aims to increase the vertical flow efficacy by adding one or more new layers of marine sands, silty loam soils, fly ash, or zeolite. A specific study of a pig slurry filtrate will be realized to determine the capacity of each material to reduce pig slurry pollution loads. Two criteria determined the selection of the materials. First, they had to be low-cost to make them technically and financially sustainable and induce big and small farmers to install an in situ treatment plant. Second, the richness of the materials in very fine mineral constituents (ferric anion and silica) makes them more active in solution and gives them high adsorbency [11].

Fly ash is rich in silica, according to Miricioiu [12], so it can be considered a potential raw material for synthesizing nanoporous materials, such as zeolites or mesoporous silica. It also has a high adsorbency potential, making it ideal for wastewater treatment, and its direct use can significantly reduce environmental damage due to its disposal [13].

Our focus was to find a new layer to add to our vertically constructed wetland’s flow to improve efficiency, study how the pig slurry reacted to the different natural materials, and compare the results with the CW. Various authors [14,15] studied clogging, percolation flow rate, long-term clogging, and rest period and found that a CW can operate for 15 years. Clogging is inevitable, but a good pretreatment can resolve it, and in this research, the slurry had been pretreated in different scenarios.

The waste from the concentrated slurry was concentrated again using EVACOLD equipment to derive a high-nutrient fertilizer.

2. Materials and Methods

2.1. Design of Experimental Device

The experimental device consisted of a glass column 10 cm in diameter and 50 cm in height as it shown in Figure 1. The effective height of the filter bed was 30 cm, 70% of which was used for the filter material (H material = 20 cm) and 30% for the raw pig slurry (H effluent = 10 cm). This column was fed from the top by adding around 800 mL of liquid pig slurry, corresponding to the 30% of the effective height of the filter bed at ambient temperature. This volume of pig slurry was left to flow through the filter materials, and the method used was based on slow filtration [16]. The inflow and outflow rates did not depend on time or any other parameter [17]. Thus, the slurry passed under a constant load through the filter bed (10 cm diameter and 20 cm in height). The upper part of the
column (a) was open to maintain water flow, and the bottom of the column was closed with a porous plate.

Every 24 h, we added the same volume of pig slurry under the same conditions for three days. The pig slurry was collected and analyzed after every treatment cycle. The treated slurry was sampled from the filter outlet (b).

**Figure 1.** Experimental device.

### 2.2. Pig Slurry Sample Collection and Analysis

Pig slurry was obtained from the main collector of a pig farm in Alhama de Murcia in southeastern Spain. On this farm, the slurry was pretreated in a five-stage process: separation, vertical decantation, first filtration (1000 µm), second filtration (250 µm), and horizontal decantation. The pretreated liquid fraction was then sent to a CW treatment plant. The volume of pig slurry required for this research was sampled from the CW entrance points.

This sample was transported directly to the laboratory and stored at 4 °C. Later, only the liquid fraction was used for analysis. The pH and EC were measured by a laboratory research-grade benchtop pH/mV and EC/TDS/Salinity/Resistivity Meter-HI5521.

Kjeldahl nitrogen (KN) was determined by a modified Kjeldahl method [18] using 1 mL of pig slurry in the digestion. Ammonium nitrogen (NH₄⁺–N) was determined by steam distillation and titration with HCl 0.1 N. Total nitrogen (TN) included organic and inorganic forms (Kjeldahl nitrogen plus nitrites and nitrate forms). Total phosphorus (TP) was photometrically determined as molybdenum blue after acidic hydrolysis and oxidation at 120 °C (Macherey–Nagel GmbH & Co. K G. Nanocolor Test; ref. 985-055, Dürren, Germany). Potassium (K⁺) was determined using an atomic absorption spectrometer (PerkinElmer AA-Analyst, 800, Jyväskylä, Finland).

Total suspended solids (TSS) were filtered through a weighed standard glass–fiber filter, and the residue retained in the filter was dried to a constant weight at 105 °C (2440-D method, APHA–AWWAWEF 2012). Biochemical oxygen demand in five days (BOD₅) was determined by manometer OXITOP WTW equipment (Darmstadt, Germany). Chemical oxygen demand (COD) was determined by photometric determination of the chromium (III) concentration after 2 h of oxidation with potassium dichromate/sulfuric acid and silver sulfate at 148 °C (Macherey–Nagel GmbH & Co. KG. Nano color Test, Ref 985 028/29, Weilheim, Germany), (DIN 38 409-H41-1, DIN ISO 15 705-H45).
Anions were analyzed by high-performance ion chromatography (IC) (Metrohm, model 861, Metrohm, Herisau, Switzerland), and cations were determined using an atomic absorption spectrometer (PerkinElmer AA-Analyst, 800, Perkin Elmer, Ueberlingen, Germany). Heavy metals were analyzed using inductively coupled plasma mass spectrometry (ICP–MS), using Agilent 7900 (Santa Clara, California, United States).

Different analysis techniques were performed for the filter substrates: particle size analysis by laser diffraction using MASTERSIZER (Malvern, United Kingdom) equipment (reference 2000LF), chemical analysis by X-ray fluorescence technique, and mineralogical analysis by X-ray diffraction (XRD).

2.3. Characterization of the Filtration Materials

The materials used for filtration were four soils, two marine sands, zeolite, and fly ash. Two types of soil were collected from a pottery company in the Alicante region. After fabrication, the soils lost their principal characteristics and could not be recycled so returning them to nature was the only way to eliminate soil waste. The choice of this material was justified because of the abundance of these soils in the region. It met the selection criteria of being more active in solution, being highly adsorbent power [11], and containing ferric ions.

The marine sand was collected along the Mediterranean coast of La Manga, washed with distilled water, and dried at 40 °C for 48 h.

Natural zeolite was purchased from ZeoCat, (Barcelone, Spain) (reference 1217-10-3), and the fly ash was purchased from a Barcelona cemetery.

All the materials had a basic pH between 9.02 and 9.96, except fly ash which was considered very basic (12.10) Table 1. The electrical conductivity of the two sands, soil 2 and soil 4, and zeolite was very low, varying between 0.1 and 0.3 ms cm⁻¹; soil 1 and soil 3 had high conductivity (1.61 and 2.29 ms cm⁻¹, respectively), while fly ash had the highest EC of 6.30 ms cm⁻¹. The pH and EC of the filter material are very important because they directly affect the pH and EC of the filtered effluent [19].

| Material       | Sand 1 | Sand 2 | Soil 1 | Soil 2 | Soil 3 | Soil 4 | Fly Ash | Zeolite |
|----------------|--------|--------|--------|--------|--------|--------|---------|---------|
| pH             | 9.69   | 9.52   | 8.60   | 9.10   | 8.46   | 8.42   | 12.10   | 9.02    |
| EC (ms cm⁻¹)   | 0.10   | 0.35   | 1.61   | 0.46   | 2.29   | 0.39   | 6.30    | 0.30    |

Size distribution curves were established by laser diffraction, representing the particles size of each material Figure 2. The results indicated that sand 1 and sand 2 had almost the same particle size, 150 µm, with a uniform coefficient of 1.67 and 1.55, respectively. Soil 1, 2, and 3 were silt loam soils, while soil 4 was a silt soil. Their particle size varied between 20 and 50 µm.

Figure 3 shows the mineralogy of the filter materials. The two sands contained various chemical compounds, the most significant concentrations of which were silica (SiO₂) and calcite (CaCO₃) for both, as described in the mineralogical analysis in Table 2.

X-ray spectra analysis showed that the soils were mostly composed of quartz, followed by muscovite. The chemical composition of soils 1–4 consisted principally of silica in quartz and substantial amounts of alumina, calcium oxide, and ferric oxide.

The first component of the fly ash, as shown in Figure 3, is mullite (Al₄.5Si₁.5O₉.75), which presented the highest percentage of 57%. In the second position was quartz (SiO₂) 24%, followed by gypsum (CaSO₄.2H₂O) 9%. According to El Fadel and Kim, the two high peaks are explained by the coal mineralogy of the fly ash [20,21]. Fly ash had a total of elements percentages ∑ SiO₂%+Al₂O₃%+Fe₂O₃% = 86.35%, which was classified among the silicon-aluminum ash, Class F, according to Coal Ash [21] and ATSM [22] Standards.
Figure 2. Cont.
Figure 2. Particle size distribution curves of the filtration materials.
Quartz (SiO$_2$) presented the highest value in zeolite mineralogy (72%), followed by aluminum oxide (Al$_2$O$_3$) (12%), while magnesium oxide (MgO) presented the lowest value (1.20%). The two peaks explained the natural aluminosilicate origin of the zeolite [23]. Based on the chemical composition of the zeolite as shown in Table 2, the silica-to-alumina ratio was 5.382, making it a Faujasite zeolite. According to Martinez [24] standards, this type has larger zeolitic pores (0.74 nm) [25].

![X-ray diffraction pattern of the filter materials.](image)

**Figure 3.** X-ray diffraction pattern of the filter materials.

**Table 2.** Geochemical composition of filter materials (%).

| Compounds | Sand 1 | Sand 2 | Soil 1 | Soil 2 | Soil 3 | Soil 4 | Fly Ash | Zeolite |
|-----------|--------|--------|--------|--------|--------|--------|---------|---------|
| SiO$_2$   | 34.5   | 32.9   | 37.3   | 48.9   | 48.6   | 41.1   | 40.9    | 64.7    |
| Al$_2$O$_3$| 1.36   | 2.34   | 12.5   | 17.5   | 18.1   | 14.9   | 26.5    | 12      |
| Fe$_2$O$_3$| 2.79   | 9.18   | 5.23   | 8.55   | 8.27   | 6.68   | 18.9    | 1.43    |
| CaO       | 34.5   | 31.2   | 19.8   | 5.89   | 5.69   | 14.5   | 6.01    | 4.12    |
| MgO       | 1.64   | 1.27   | 2.72   | 2.59   | 2.81   | 1.47   | 0.94    | 0.94    |
| SO$_3$    | 0.23   | 0.22   | 0.14   | 0.24   | 0.40   | 0.25   | 1.74    | 0.04    |
| K$_2$O    | 0.30   | 0.52   | 2.81   | 0.06   | 5.16   | 3.10   | 2.04    | 2.65    |

### 3. Results and Discussion

#### 3.1. Physical Chemical Characterization of Raw Pig Slurry

The characteristics of animal manure vary considerably among and within species according to country, farm, production method, feed composition, and water consumption [26]. Table 3 presents the physicochemical results of the raw and treated pig slurry by different materials.

The effluent had a pH of 7.54, which is normal for pig slurry. According to Antezena, the pH of animal slurry ranges from 6.3 to 8 on Spanish commercial farms [27].

The pig slurry’s EC depended on the pig’s age and type (growing pigs and gestating sows had a higher EC than for lactating sows and nursery piglets) and storage time, thereby enhancing drying and mineralization of the slurry [26]. Differences in the concentration of proteins and minerals in the diet may also have contributed to differences in EC [28,29].

Our effluent had a low conductivity of 7.4 ms cm$^{-1}$. According to Antezena [27], the national commercial farm range [30,31] is 6.59–53.5 ms cm$^{-1}$ for growing pigs, which means that the slurry was at the low end, and there was a high possibility that the use of cleaning water diluted our effluent.
The raw PS turbidity was 2000 NTU, signifying solids and the presence of organic matter, which gave a good idea of the pollution level: the TSS, COD, and BOD\textsubscript{5} were 80.90, 7, and 4 g L\textsuperscript{-1}, respectively, which signified that the piggery wastewater contained large amounts of organic matter.

The Kjeldahl nitrogen comprised nitrogen in ammonic and organic form, excluding nitrous forms (nitrites) and nitric form (nitrates), and the origin of organic nitrogen (urea).

Table 3 shows the results obtained after the passage of raw pig slurry through the filter materials. As the water passed through the filter, a thin biological film built up on the surface of the materials: solid particles and natural microorganisms accumulated in it and contributed to the slow-flow filtration. The biofilm made the filter very effective because it contributed to the slow-flow filtration. The biofilm made the filter very effective because it contributed to the slow-flow filtration. The biofilm made the filter very effective because it contributed to the slow-flow filtration. The biofilm made the filter very effective because it contributed to the slow-flow filtration.

The increase in pH values of the slurry after different filtration tests was explained by the presence of basic ions. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33]. The increase in pH was linked to the alkaline filter media, according to El Houati [33].

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loamy materials and by the low conductivity of the filter materials Sand 1, Sand 2, Soil 1, Soil 3, and Soil 4.

Increasing values were directly related to the electrical conductivity of the filter materials. Referring to Table 1, fly ash had a high conductivity compared to the other materials 6.30 ms cm$^{-1}$, which explained the high conductivity of the filtered effluent 9.44 ms cm$^{-1}$. The same was true for Soil 3 and 4.

Table 3 shows that a constructed wetland reduced EC by only 14%, the material that had a highly significant effect on reducing the EC is zeolite (65%). Total suspended solids achieved an elimination rate between 82 and 99.99%. COD reduction achieved an elimination rate that ranged between 72 and 90%, and BOD$_5$ reduction was 99.99%.

The physical-chemical characteristics of the materials explain reductions in organic loads and TSS. Because the particle sizes were 150–10 µm, the materials were ideal for capturing and retaining suspended solids. The small particles size increased the exchange surface between the effluent and material, thus easily trapping TSS in the pores of the adsorbent, according to Setyobudiarso [38]. As more organic substances from the effluent became trapped in the adsorbent pores, the BOD$_5$ and COD content fell [38]. This reduction was mainly due to filtration, sedimentation, and sieving at the filter bed [39]. Moreover, the high concentration of silica (>35%) was able to absorb solids suspended in water [20]. Its strong polarity and mineral elements, particularly ferrous ions (Fe$^{2+}$), neutralized the negative charges on the organic matter [40].

Compared to filtration with CWs, all the materials achieved an equal or better reduction of TSS, COD, and BOD$_5$. Only the zeolite achieved a high elimination rate (around 99.99%) of the three parameters previously mentioned. The oxidation of organic nitrogen explained this reduction of Kjeldahl nitrogen to oxidized nitrogen (NOx). Joint denitrification can occur simultaneously in areas of the filter bed that became anoxic [41] and was further stimulated by lime (CaO) present in the filter materials.

The pH of the effluent and filtration materials was very important for nitrifying bacteria, which required a pH between 7.4 and 9 for Nitrosomonas, and between 8.5 and 9.1 for Nitrobacter. According to Biod and EPA [42,43], this explained the high reduction of nitrogen by the four soils and zeolite.

However, the low reduction of nitrogen by Sand 1, Sand 2, and fly ash was explained by their high pH: 9.69, 9.52, 12.10, respectively Table 1. Furthermore, the pH of the filtered effluents were 8.92, 8.98, and 12.02. According to CPW [44] the closer the pH was to 9.6, the closer nitrification came to 0.

The maximum nitrogen removal by zeolite was explained by its large specific surface area, ideally suited for autotrophic bacterial colonies that convert ammonia to nitrite and nitrite to nitrate through aerobic and anaerobic nitrification. Zeolite allowed a very good optimal nitrification level [40,41].

Sand 2 could reduce the same as the CW, while soils 1–4, fly ash, and zeolite achieved a high reduction rate. The high reduction of almost 99.99% was obtained by zeolite, which was 65% higher than the CW.

3.2. Micronutrient Results in Raw and Filtered Pig Slurry

Table 4 shows the micronutrients Mn, Cu, Zn, Fe in raw and filtered pig slurry and the high percentage of their reduction.

Iron and zinc ions present high values in raw pig slurry, and all materials had a removal rate of 99.99%, except fly ash, which reduced iron ions by only 80%.

Copper and manganese ion concentrations were 106 and 190 µg L$^{-1}$, respectively, and all materials achieved a high reduction between 50 and 99.99% for cupric ions. Manganese reduction by all materials was 80 to 99.99%, except soil 3 and soil 4, which only reduced 10%.

The CW released a high content of manganese as it reduced copper, zinc, and iron. Compared to the other materials, zeolite was the only material with a reduction rate of almost 99.99% for all micronutrients.
Table 4. Micronutrients of raw and filtered pig slurry.

|          | Mn (µg L\(^{-1}\)) | Cu (µg L\(^{-1}\)) | Zn (µg L\(^{-1}\)) | Fe (µg L\(^{-1}\)) |
|----------|--------------------|--------------------|--------------------|--------------------|
| PS       | 190 ±0.00          | 106 ±0.01          | 451 ±0.01          | 783 ±0.01          |
| Sand 1   | 23 ±0.00           | 56 ±0.01           | BDL * ±0.00        | BDL * ±0.00        |
| % reduction | 87.74%            | 46.60%            | 99.99%            | 99.99%            |
| Sand 2   | 28 ±0.00           | 333 ±0.12          | BDL * ±0.00        | BDL * ±0.00        |
| % reduction | 85.11%            | -214.15%          | 99.99%            | 99.99%            |
| Soil 1   | 31 ±0.00           | 63 ±0.01           | BDL * ±0.00        | BDL * ±0.00        |
| % reduction | 84.21%            | 40.28%            | 99.99%            | 99.99%            |
| Soil 2   | 9 ±0.00            | BDL * ±0.00        | BDL * ±0.00        | BDL * ±0.00        |
| % reduction | 95.26%            | 99.99%            | 99.99%            | 99.99%            |
| Soil 3   | 173 ±0.00          | 13 ±0.00           | BDL * ±0.00        | BDL * ±0.00        |
| % reduction | 8.95%             | 87.45%            | 99.99%            | 99.99%            |
| Soil 4   | 171 ±0.02          | BDL * ±0.00        | BDL * ±0.00        | BDL * ±0.00        |
| % reduction | 10.53%            | 99.99%            | 99.99%            | 99.99%            |
| Fly Ash  | 11 ±0.00           | BDL * ±0.00        | BDL * ±0.00        | 213 ±0.00          |
| % reduction | 94.74%            | 99.99%            | 99.99%            | 72.80%            |
| Zeolite  | BDL * ±0.00        | BDL * ±0.00        | BDL * ±0.00        | 9 ±0.00            |
| % reduction | 99.99%            | 99.99%            | 99.99%            | 98.85%            |
| CW       | 601 ±0.02          | 40 ±0.00           | 11 ±0.00           | 11 ±0.00           |
| % reduction | -215.79%          | 62.26%            | 97.78%            | 98.72%            |

Below detection limit (BDL)*: Mn: 0.00033 mg L\(^{-1}\), Cu: 0.0003 mg L\(^{-1}\), Zn: 0.00126 mg L\(^{-1}\), Fe: 0.00045 mg L\(^{-1}\).

The ferric and aluminum oxides in the filtration materials made them good adsorbents for metallic ions [45]. Zeolite has a high ion exchange capacity and ability to remove dissolved heavy metals in an aqueous solution, which explains the high reduction of micronutrients after contact between the pig slurry and filtration materials [46].

3.3. Heavy Metal Reduction

Table 5 presents the metallic elements (Pb, Co, Ni, Cr, and Al) in raw and filtered PS. In the raw slurry, lead, cobalt, nickel, chromium, and aluminum ions were present with concentrations of 1, 1, 11, 0.8, and 38 µg L\(^{-1}\), respectively. Aluminum ions recorded the highest concentration and were strongly reduced by all materials with a high reduction rate of 99 %, except for the CW (74%).

Nickel ions had a low concentration of 11 µg L\(^{-1}\). Sand 1, soil 2, and soil 3 reduced it while fly ash and zeolite eliminated it. Soil 1, soil 4, and sand 2, in contrast, released more nickel ions, which may have been related to the contamination of those soils.

Chromium had a low concentration of 0.8 µg L\(^{-1}\). The sands, soils 1, 2, and 4, and fly ash reduced it, soil 3 and zeolite eliminated it.

The two sands released lead into the effluent with a concentration of 9 µg L\(^{-1}\). Nickel had a low concentration, 11 µg L\(^{-1}\), but sand 2, soil 4, and the CW released more with concentrations 60, 20, and 40 µg L\(^{-1}\), respectively, possibly because of contamination by those ions.

Table 5 shows that pig slurry treatment by the different filter materials further reduced heavy metals. The variable removal rate was due to the ionic form of each metal, the ability of each bacterium to consume the metal, and the differing physicochemical conditions of each organism.
### Table 5. Heavy metals of raw and filtered pig slurry.

|          | Pb (µg L⁻¹) | Co (µg L⁻¹) | Ni (µg L⁻¹) | Cr (µg L⁻¹) | Al (µg L⁻¹) |
|----------|-------------|-------------|-------------|-------------|-------------|
| PS       | 1 ±0.00     | 1 ±0.00     | 11 ±0.00    | 0.8 ±0.00   | 38 ±0.00    |
| Sand 1   | 9 ±0.00     | 10 ±0.00    | BDL *       | 0.9 ±0.00   | BDL *       |
| % reduction | −727%     | −550%      | 99.99%      | −13%        | 99.99%      |
| Sand 2   | 9 ±0.00     | 9 ±0.00     | 60 ±0.00    | 0.9 ±0.00   | BDL *       |
| % reduction | −718%     | −542%      | −440%       | −12.50%     | 99.99%      |
| Soil 1   | BDL *       | BDL *       | 14 ±0.00    | 1.8 ±0.00   | BDL *       |
| % reduction | 99.99%     | 99.99%     | −26.13%     | −125%       | 99.99%      |
| Soil 2   | BDL *       | BDL *       | 4 ±0.00     | 1.1 ±0.00   | BDL *       |
| % reduction | 99.99%     | 99.99%     | 65.77%      | −37.50%     | 99.99%      |
| Soil 3   | BDL *       | BDL *       | 7 ±0.00     | 0.9 ±0.00   | BDL *       |
| % reduction | 99.99%     | 99.99%     | 32.16%      | −12.50%     | 99.99%      |
| Soil 4   | BDL *       | BDL *       | 20 ±0.00    | 1.8 ±0.00   | BDL *       |
| % reduction | 99.99%     | 99.99%     | −87.39%     | −125%       | 99.99%      |
| Fly Ash  | BDL *       | BDL *       | 0.00        | BDL *       | 4.8 ±0.00   |
| % reduction | 99.99%     | 99.99%     | 99.99%      | −500%       | 99.99%      |
| Zeolite  | BDL *       | BDL *       | BDL *       | BDL *       | BDL *       |
| % reduction | 99.99%     | 99.99%     | 99.99%      | 99.99%      | 99.99%      |
| CW       | BDL *       | BDL *       | 40 ±0.00    | 3 ±0.00     | 10 ±0.00    |
| % reduction | 99.99%     | 99.99%     | −266%       | −325%       | 73.75%      |

Below detection limit (BDL*); Pb, 0.00004 mg L⁻¹; Ni, 0.00051 mg L⁻¹; Cr, 0.00006 mg L⁻¹; Co, 0.00008 mg L⁻¹; Al, 0.0004 mg L⁻¹.

Indeed, with the richness of silica in the sand, the surface hydroxyl groups were formed by hydration, which allowed the adsorption of metallic cations [47]. Iron oxides and aluminum oxides in fly ash (% $\sum Al_2O_3 + Fe_2O_3 = 45.41\%$) and soils (% $\sum Al_2O_3 + Fe_2O_3 = soils 1, 17.7\%; soil 2, 26.1\%; soil 3, 26.4\%; soil 4, 21.6\%$) made them good adsorbents with a high metallic ion retention [45].

Zeolite has been investigated for its ion exchange capacity and its high ability to remove heavy metals dissolved in an aqueous solution through ion exchange [48]. This explains the high removal of all metals present in the raw pig slurry with an elimination rate of 99.99%.

#### 3.4. Macronutrient Removal

As presented in Table 6, the two different sands reduced nitrogen at the same rate of 9%. Soil 1, soil 2, soil 3, soil 4, fly ash, and the CW reduced it by 51, 64, 58, 61, 39, and 30%, respectively. The largest reduction was obtained from zeolite, 75%.
Table 6. Macronutrients of raw and filtered pig slurry.

|                | N (mg L⁻¹) | Na⁺ (mg L⁻¹) | K⁺ (mg L⁻¹) | Ca²⁺ (mg L⁻¹) | Mg²⁺ (mg L⁻¹) | P (mg L⁻¹) |
|----------------|------------|--------------|-------------|---------------|---------------|------------|
| PS             | 150 ± 0.6  | 120 ± 0.3    | 125 ± 1.1   | 105 ± 1.7     | 104 ± 1.2     | 20.11 ± 0.0 |
| Sand 1         | 136 ± 0.3  | 120 ± 0.3    | 119 ± 0.6   | 40.5 ± 1.6    | 105 ± 0.1     | 1.25 ± 0.0  |
| % reduction    | 9%         | −1%          | 5%          | 61%           | −1%           | 94%        |
| Sand 2         | 136 ± 0.6  | 120 ± 0.6    | 120 ± 1.7   | 33.67 ± 1.2   | 105 ± 0.1     | 1.73 ± 0.0  |
| % reduction    | 9%         | 0%           | 4%          | 67.94%        | −1%           | 91%        |
| Soil 1         | 74 ± 0.6   | 106 ± 0.6    | 98 ± 2.7    | 129 ± 2.0     | 120 ± 0.1     | 0.31 ± 0.0  |
| % reduction    | 51%        | 11%          | 21.33%      | −22.86%       | −15%          | 98%        |
| Soil 2         | 74 ± 0.3   | 195 ± 0.6    | 85 ± 1.1    | 120 ± 0.0     | 102 ± 0.7     | 0 ± 0.0     |
| % reduction    | 64%        | −63%         | 32.05%      | −14.29%       | 2%            | 99.99%      |
| Soil 3         | 64 ± 0.3   | 260 ± 0.5    | 108 ± 1.5   | 180 ± 0.3     | 173 ± 0.2     | 0 ± 0.0     |
| % reduction    | 58%        | −117%        | 13.60%      | −71.43%       | −66%          | 99.99%      |
| Soil 4         | 58 ± 0.2   | 290 ± 0.6    | 107 ± 1.1   | 183 ± 0.1     | 225 ± 0.0     | 0.27 ± 0.0  |
| % reduction    | 61%        | −142%        | 14.40%      | −74.29%       | −116%         | 99%        |
| Fly Ash        | 92 ± 0.0   | 150 ± 0.0    | 170 ± 1.1   | 175 ± 0.5     | 11 ± 0.0      | 0 ± 0.0     |
| % reduction    | 39%        | −25%         | −36%        | −66.98%       | 89%           | 99.99%      |
| Zeolite        | 38 ± 0.3   | 70 ± 1.1     | 40 ± 0.9    | 132 ± 0.3     | 101 ± 0.3     | 0.17 ± 0.0  |
| % reduction    | 75%        | 42%          | 67.73%      | −26.35%       | 3%            | 99%        |
| CW             | 105 ± 0.6  | 134 ± 0.3    | 132 ± 0.9   | 24 ± 0.1      | 30.03 ± 0.1   | 1.08 ± 0.0  |
| % reduction    | 30%        | −12%         | −6.13%      | 77.02%        | 71%           | 95%        |

The eight materials were rich in aluminum oxides, iron oxides, and lime (Al₂O₃, Fe₂O₃, and CaO, respectively), considered coagulants and reagents for the physicochemical removal of phosphorus because they precipitated out ferrous phosphate and lime phosphate [49–52]. Those scenarios explain the high elimination rate of phosphorus.

The water hardness was caused by calcium and magnesium salts [53]. Only the two sands and the CW reduced it, when it achieved 1000 mg L⁻¹ using soil 3, soil 4, and fly ash. Those salts were dissolved from filter materials initially formed by lime, dolomite (CaMg(CO₃)₂), and magnesite (MgCO₃).

The materials were divided into three groups according to potassium levels: The first group (sand 1 and sand 2) had no effect as potassium held the same values in filtered and raw effluent. The second group (fly ash) doubled the potassium in the effluent, related to the richness of potassium in fly ash. The third group (all the soils and zeolite) potentially reduced the potassium, and the organic matter particles held the potassium ions in an exchangeable or available form. According to Charles [54], potassium does not leach from silty or clayey soils and is held between soil particles more tightly and can be stored, which explained the potassium reduction with the four silty soils. According to ion selectivity [55], zeolite had high potassium absorbency due to ion exchange and exchangeable cations.
The maximum removal rate of sodium was recorded by zeolite then by soil 1. Sand 1 and sand 2 did not have any significant effect. Soils 2–4 released more sodium in the effluent. Zeolite had a high cation exchange capacity and selectivity due to its high porosity and sieving properties [56]. It is reported to have replaced sodium ions from the solution with calcium [57], which explains the sodium reduction and calcium increment.

The constructed wetland achieved a high reduction of some micronutrients (calcium, magnesium, and phosphorus) while it released sodium and had no significant effect on potassium. Zeolite reacted oppositely to the CW by reducing sodium and potassium to a high degree and magnesium slightly as it released calcium. The CW and zeolite were complementary.

Results data obtained in this research shows that adding a new material layer to the CW can increase its quality. It should be noted that the experimental results do not have a control experiment showing the new layer performance compared to the normal CW. Therefore, new research to compare the CWs with and without the new layer is recommended.

4. Conclusions

Richness in silica and metallic oxides and small particle size were the reasons for the good results from the different filter materials.

In summary, filtration by marine sands, loamy soils, fly ash, and zeolite generally reduced physical-chemical loads, micro-and macronutrients, and heavy metals with different removal rates. All the materials achieved a high elimination of chemical pollution loads: up to 74% for COD, 75% for BOD$_5$, 91% for TSS, and 89% for nitrogen, except for the two sands and fly ash, which achieves 24 and 32%, respectively. Concerning micro-and macronutrients and heavy metals, some materials proved their ability to adsorb ions and release others simultaneously.

Comparing the adsorption and release percentages, zeolite proved to be the best material to be integrated into the construction of the wetland. It adsorbed pig slurry pollution loads with high percentages while it released ions such as calcium (Ca$^{2+}$ 199 mg L$^{-1}$). The CW proved its ability to reduce calcium; therefore, adding a 21 cm layer of zeolite to the CW will raise its efficiency as a pig slurry filtration system.

**Author Contributions:** Conceptualization, O.E.b. and J.A.A.; methodology, O.E.b. and A.G.-V.; validation, T.F. and Á.F.; formal analysis, O.E.b. and J.A.A.; investigation, O.E.b. and A.G.-V.; resources, J.A.A.; data curation, O.E.b. and J.A.A.; writing—original draft preparation, J.A.A. and O.E.b.; writing—review and editing, O.E.b. and J.A.A.; visualization, O.E.b. and J.A.A.; supervision, J.A.A. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by GARSÁ Research group.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Written informed consent was obtained from the participants and guardians of underage participants to publish this paper.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** We would like to thank the researchers involved in the materials collection and special thanks to the director of CEMEX company, Agustin Garcia Huertas, for facilitating the process to afford the fly ash.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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