

## Article

# Treatment of Agricultural Waste Using a Combination of Anaerobic, Aerobic, and Adsorption Processes

Kyriaki Trouli, Spyros Dokianakis, Evangelia Vasilaki and Nikos Katsarakis \*

Center of Materials Technology and Photonics, Hellenic Mediterranean University, 714 10 Heraklion, Greece

\* Correspondence: katsan@hmu.gr; Tel.: +30-281-0379-300

**Abstract:** The generation of waste in agricultural and livestock industries, followed by inadequate treatment and uncontrolled disposal to natural recipients, results in significant environmental pollution. Thus, the efficient and integrated management of high-organic-load waste produced in such activities is a key factor for sustainability and the protection of aqueous matrices. In this work, we investigate an integrated management approach for the treatment of agricultural, high-organic-load waste via a combination of processes, with an ultimate goal to improve the characteristics of the final waste and enhance the valorization of the nutrients contained in it. Towards this direction, a waste mixture comprising pig waste, cheese dairy, and food residues was sequentially treated in a laboratory scale by anaerobic digestion, followed by activated sludge (aerobic–anoxic treatment), and last by adsorption using natural zeolite. The efficiency of two different adsorption routes was examined (magnetically agitated zeolite or packed zeolite column), while the effect of the granule sizes of zeolite (0–1 mm or 1.5–3 mm) was also evaluated with regards to the remediation of the final effluent. Excellent adsorption capacities were observed in all cases, with the larger-sized zeolite exhibiting a superior performance, while the granule size of zeolite significantly affected the lifetime of the packed columns, as the smaller-sized zeolite columns reached their saturation point faster than the larger-sized zeolite analogue. The average ammonium nitrogen removal in the column experiment was ~92%, while total phosphorus was ~68%, respectively. Overall, an almost complete remediation of the final effluent was observed when compared with the physicochemical parameters of the initial waste, with a ~96% chemical oxygen demand, ~79% total nitrogen, ~96% total phosphorus, and ~82% phenols concentration decrease, signifying the high performance of the sequential treatment strategy proposed herein.

**Keywords:** wastewater treatment; anaerobic digestion; activated sludge; natural zeolite; adsorption; clinoptilolite



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## 1. Introduction

The depletion of natural water suitable for irrigation and stock-raising purposes, either due to mismanagement or natural causes, is one of the most critical industrial problems we have to face during the last decades. Towards the direction of more readily available alternative water sources, the reuse of wastewater generated by the agricultural and stock-raising industries could constitute a promising sustainable and zero-waste approach [1]. Furthermore, the vast majority of livestock and agricultural industries is in operation without integrated sewage treatment plant and disposal areas, while many industries are characterized by seasonal operation and low capacity. Wastewater generated from these agricultural and stock-raising industries, such as piggery waste, cheese dairy, and food residues are characterized as high strength, with high ammonium nitrogen, total phosphorus, chemical oxygen demand (COD), and biological oxygen demand (BOD) values [2,3]. As a result, the inadequate treatment and the unregulated disposal of the generated waste to natural recipients is the cause of significant environmental pollution. Thus, it is clear,

that before the reuse of agro-industrial wastewater, the removal of hazardous pollutants that could potentially pose environmental and health threats is imperative.

Different strategies have been proposed in the literature towards the remediation of agro-industrial wastewater, namely, biological and physicochemical routes, advanced oxidation processes, or hybrid systems combining two or more of the aforementioned techniques [2–4]. However, it is widely reported that the treated wastewater following the above approaches still contains significant concentrations of contaminants hindering their further reuse, while, in some reports, these concentrations are above the legal limits even for disposal [5–7]. In addition, more effective treatment methods such as filtration and reverse osmosis are characterized by complexity and high operational costs, rendering them impractical [8]. It is clear that in order for the treatment of high-strength waste to be economically viable, added value byproducts have to be generated during this process. The production of biogas through anaerobic digestion, as well as solid and liquid fertilizers through the combination of biological and ultrafiltration processes constitute promising ways to deal with the operational costs of the waste treatment [1]. Similarly, there is a lot of interest towards the exploitation of the nutrients (N, P, and K) that are usually present in waste of high organic strength, and specifically, in the liquid digestate generated through the anaerobic digestion processes.

Recently, wastewater remediation using zeolite, a natural and low-cost adsorbent, has attracted significant scientific attention [9–11]. However, the literature reports referring to the treatment of agro-industrial wastewater using zeolite are scarce. In a representative report, Aly et al. [12,13] tunneled olive mill wastewater through successive columns packed with different materials. The first column was packed with gravel, the second with sand, and the third with a mixture of cotton and clinoptilolite. The authors reported a high removal of the contaminants under consideration (potassium, nitrates, phosphorus, and total phenols) in the zeolite column. Huang et al. [14] correlated important experimental parameters, such as the zeolite concentration, pH, and competitive ions, with the adsorption efficiency of ammonium from simulated swine wastewater. The effect of the above parameters was found significant with removal rates varying from 40% to 95%. The treatment of wastewater derived from dairy industries using zeolite has been the focus of a number of studies [15,16] examining important pollution indexes, i.e., COD, phosphorus, ammonium, nitrate nitrogen, and phosphate. The authors reported varying efficiencies of the process based on the investigated parameter. For instance, Samkuty and Gough [16] reported only ~30% COD removal using natural zeolite when compared with other investigated adsorbents that exhibited up to 93% COD removal. However, zeolite was reported as a promising candidate for the removal of ammonium from dairy waste, with higher removal values, that were, however, influenced by the pH value of the treated waste [17]. Recently, Vayenas et al. [5] evaluated natural zeolite of various granular sizes as adsorbent for the removal of ammonium from artificial wastewater and secondary cheese whey. The authors reported no significant effect of the granulometry of the ammonium removal efficiency; however, smaller particles exhibited a faster response. In addition, ~40% COD removal rates under optimized conditions were observed, while for phosphorus, fast saturation of zeolite after 1 day of operation was reported.

However, the aforementioned studies focus only on simulated or real wastewater originating from a single source, and not on complex waste mixtures which are representative of the real conditions in wastewater management plants. In addition, during the last decades, huge amounts of waste has been produced by food industries (about 30 million tons of waste per year in Europe), but also from the disposal of food from hotels, restaurants, and households due to hygiene rules (expired food). Moreover, in Greece, food residues are not treated before disposal, but instead they are accumulated in landfills, where they decompose releasing methane in the atmosphere, which is considered one of the most powerful greenhouse gases. Food waste can be recovered and diverted to animal feed whenever possible. However, there is a wide disparity in government policies and regulations among countries, a phenomenon that hinders the exploitation of food

waste towards animal feed. According to our knowledge, the European Union prohibits the use of catering waste or kitchen scraps as farm animal feed in order to minimize the risk of transmission of animal diseases [18]. However, food waste is significantly rich in hydrocarbons (cellulose, hemicelluloses, starch, and lignin) that have great potential for the generation of energy (electricity and heat) and the production of added-value products (bio-oil, biogas, fertilizers, etc.). Policies and regulations must be reformed using a more holistic approach that will mandate the recovery and recycling of greater amounts of these valuable nutrients from various food waste streams [19]. Thus, in order to recover these resources, a very promising and acceptable policy according to the Food Recover Hierarchy, developed by the Environmental Protection Agency, is the utilization of food waste in industrial applications, such as the generation of biogas [20]. Last but not least, the evaluation of zeolite in conjunction with other treatment processes, which is expected to greatly enhance the effectiveness of the overall integrated management process, has not been evaluated, to-the-best of our knowledge, for complex waste mixtures. The aim of this study is the remediation of a mixture of high-strength, agro-industrial waste (piggery waste, cheese dairy, and food residues), via a sequential combination of treatment processes and specifically, anaerobic digestion followed by activated sludge (aerobic–anoxic treatment) and adsorption using natural zeolite (Clinoptilolite) as a final step. The efficiency of the proposed treatment strategy was systematically correlated to the granular size and concentration of the zeolite in suspensions of the waste mixture, as well as packed in columns. The proposed methodology can be efficiently applied to the remediation of complex mixtures of organic waste of high strength on an industrial level.

## 2. Materials and Methods

The waste sources for the mixture used in this work were small-scale, local industries. In particular, the liquid fraction of pig waste was supplied by a local farm located in the area of Voutes, Heraklion, Crete, while cheese whey was received from a cheese factory in Smari village in Heraklion. In addition, food waste was kindly supplied by local hotels located in the Municipality of Heraklion, and was pre-treated with solar drying, in order to eliminate water content and stabilize the microbial load, which was necessary for long-term storage. The above waste was chosen as the most representative waste from sources related to the local agricultural, farming, and urban activities of Heraklion, Crete, and were kept at  $-20\text{ }^{\circ}\text{C}$  before further use. It has to be highlighted at this point that the sample collection from each waste source was not performed only once, but waste aliquots were collected frequently from the respective industries due to storage limitations and to more properly reflect the seasonality of the waste properties that applies in real conditions. However, the composition of the investigate waste mixture was maintained constant throughout the experiments at 75% pig waste and 25% cheese whey, while 50 g of homogenized dry food waste was also added per 1 L of the above mixture.

The treatment of the waste mixture was performed in a sequential manner, meaning that the effluent of one treatment process was the influent of the following. In specific, the homogenized waste mixture was first treated by anaerobic digestion, using a 3 L volume lab-scale continuous stirred-tank reactor (CSTR), while the hydraulic retention time (HRT) was 40 days and the daily feed of the reactor was 75 mL of mixture waste, manually injected through a feeding portal. The temperature of the reactor was maintained at  $40\text{ }^{\circ}\text{C}$  via the flow of warm water through its double-walled stainless-steel jacket and the mixture waste was kept under constant mechanical stirring. The total operational time of the CSTR was 165 days; however, aliquots of the treated waste were collected every 15 days. Next, centrifugation (4000 rpm, 15 min, Hettich EBA 20, Hettich, Tuttlingen, Germany) of the effluent of the digester was performed, a process that is commonly used in industrial scale anaerobic digesters in order to separate the two fractions. Limiting the solid material ensures better operation of the following oxic–anoxic treatment, avoiding hindered aeration.

The collected liquid supernatant was employed as the influent of the activated sludge reactor. The oxic–anoxic treatment of the waste mixture was performed in an in-house constructed sequencing batch reactor (SBR) with the ability of sequential operation, both aerobically as well as anoxically, based on whether aeration was supplied to the reactor or not, respectively. The operational volume of the reactor was 500 mL, while aeration was supplied using an aeration pump. A full SBR operation cycle lasted 24 h and consisted of four discrete stages: the fill phase (1 min), during which 60 mL of the waste mixture was fed into the reaction daily, followed by the reaction phase (23 h of alternating aerobic and anoxic cycles (ratio 2:1)), where the organic load is consumed by the active biomass under controlled conditions and an amount of nitrogen is degraded through the nitrification–denitrification process. Next, the biosolids fraction was left to separate from the treated liquid under anoxic conditions and without stirring (1 h). The last stage is the draw phase, during which the supernatant liquid (60 mL) is removed via a syringe. The total duration of the operation of the SBR was 154 days. Centrifugation, under the same conditions as described above, was performed for the collected SBR liquid fraction, before storage of the supernatant at  $-20\text{ }^{\circ}\text{C}$ . The storage of the SBR effluent was necessary to ensure that a sufficient waste volume was available for the following adsorption studies.

The collected effluent of the SBR process was then thawed and was further used as the influent of the adsorption studies. Greek Clinoptilolite (supplied by a local distributor with batch number GR131024) was employed as the adsorbent material and its properties are presented in Table 1. Two different zeolite granule sizes were studied herein, a coarse, as-received zeolite with a granule size of 1.5–3 mm and its ground form with a granule size below 1 mm. Before further use, the zeolite with 1.5–3 mm granule size was repeatedly washed with deionized water, followed by drying at  $100\text{ }^{\circ}\text{C}$  overnight, as suggested in the literature [21], while the powdered zeolite was used without any further purification. Adsorption experiments were conducted using two different methodologies: magnetic stirring of the waste with the zeolite and channeling of the waste through packed zeolite columns. For the first approach, 50 mL of CSTR and SBR treated waste was magnetically stirred at room temperature with different quantities (2 g, 5 g, 7 g, and 10 g) of the coarse or the ground zeolite in conical flasks sealed with Parafilm for 24 h. To evaluate the possible effect of stirring, 50 mL of the pretreated waste was also mixed with 10 g of coarse or ground zeolite and the dispersion was left without stirring, while for comparison reasons, 50 mL of waste was also left at room temperature for 24 h in the absence of zeolite as the control sample. The waste was separated from the suspended zeolite via centrifugation for further analysis of the investigated physicochemical properties.

**Table 1.** Physicochemical characteristics of the zeolite used in this work.

Parameter	Value
Clinoptilolite group	70–85%
Surface area (BET)	40–44 $\text{m}^2\text{ g}^{-1}$
Porosity	35% (average)
Bulk density	0.8–1.1 $\text{g (cm}^3\text{)}^{-1}$
pH	6.5–7.5
Specific gravity	2.0–2.1 $\text{g (cm}^3\text{)}^{-1}$

For the packed column adsorption experiments, one Plexiglas column with an inner diameter of 8 cm and height of 16 cm was employed, in which 200 g of coarse zeolite was added. The other type of zeolite (ground) was also tested, but the low porosity resulted in the accumulation of the feed in the inlet of the column after a few days. Waste feed was added in a continuous mode by using a Shenchen 2 Syringe Pump SPLab02 (Baoding Shenchen Precision Pump Co., Ltd., Baoding, China), adjusted to 60 mL per day for the first operation cycle and increased to 72 mL per day till the end of the experiment. The effluent of the column was collected and characterized every 24 h.

The various physicochemical characteristics of the waste mixture before and after each treatment step were analyzed as follows. The value of pH of samples collected from experiments was measured by using an Orion 3 Star Thermo Scientific (Singapore) pH meter portable electrochemical analyzer, while various important parameters were quantified, i.e., total solids (TS), total suspended solids (TSS), volatile solids (VS), and volatile suspended solids (VSS), total phosphorus (TP), phosphate phosphorus (PO<sub>4</sub>-P), total nitrogen (TN), nitrite nitrogen (NO<sub>2</sub>-N), and chemical oxygen demand (COD) as proposed by standard methods [22]. The persulfate digestion method was used for the determination of total phosphorus and total nitrogen. Dissolved phenolic compounds were determined spectrophotometrically according to the Folin–Ciocalteu method [23]. Ammonium nitrogen was determined using a kit from Macherey–Nagel (Tube test NANOCOLOR Ammonium 100) and nitrate nitrogen with a kit from Hach (NO<sub>3</sub>-NtestLCK339). The composition of biogas was measured with a portable Optima7 gas analyzer (MRU GmbH, Neckarsulm, Germany). The produced biogas was collected in airtight nylon bags, which were connected to the conical flask that was collecting the effluent (Figure 1) with silicone tubes. The volume of biogas was determined via the water displacement method, by channeling the gas from the bag into a conical flask connected to a volumetric cylinder and measuring the volume for the displacement of water.



**Figure 1.** Experimental setup of the anaerobic digestion reactor used in this study.

All measurements were replicated in triplicate and the data are presented as mean  $\pm$  SD. Statistical analysis of the data was performed using Microsoft Excel (Prof. Plus 2013).

### 3. Results and Discussion

First, the physicochemical characteristics of the waste mixture before further treatment were quantified and the respective results are shown in Table 2.

**Table 2.** Physicochemical characteristics of the non-treated waste mixture.

Parameter	Value
pH	5.1–5.4
TS (g L <sup>-1</sup> )	45–60
VS (g L <sup>-1</sup> )	37–51
COD (g L <sup>-1</sup> )	71.08–76.14
TN (mg L <sup>-1</sup> )	1424–1778
TP (mg L <sup>-1</sup> )	560–593
Phenols concentration (mg L <sup>-1</sup> )	281–349

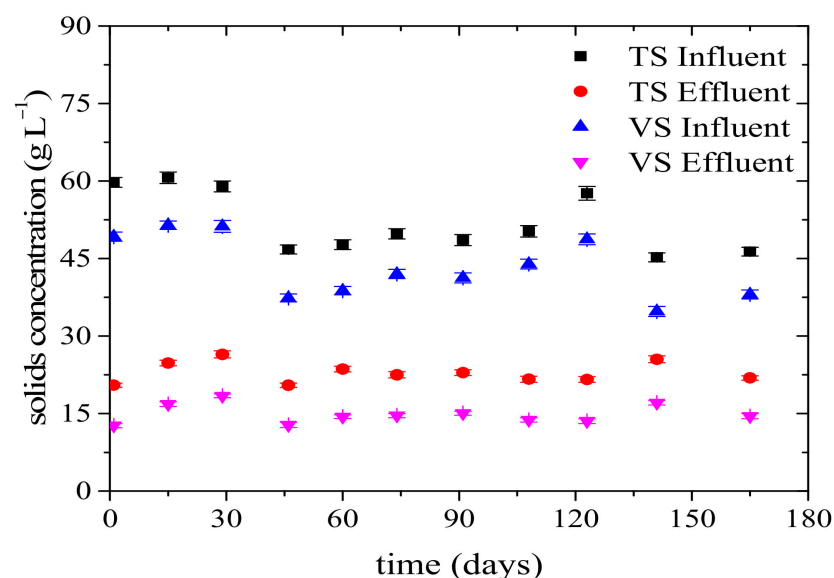


The non-treated waste exhibited high TP, TN, and COD values, signifying the high organic load of the waste mixture, results that highlight the necessity for efficient remediation before disposal. The variations observed for each physicochemical parameter are due to the fact that sampling was not performed only once in this study and thus seasonal variations of the waste properties are expected.

### 3.1. Anaerobic Digestion

The waste mixture was first treated by anaerobic digestion (Figure 1) and the most important physicochemical parameters of the effluent were monitored systematically.

The value of the pH during anaerobic digestion was found to increase after treatment, from  $5.2 \pm 0.2$  to  $7.6 \pm 0.3$ . This phenomenon is an indication of the efficient operation of the reactor, as the optimum operating pH range for the anaerobic digestion process is approximately 7. When the environment inside the reactor is acidic, the biological functions of the beneficial microorganisms are hindered, resulting in the accumulation of volatile fatty acids (VFA) which are not converted to methane and, therefore, the final stage of degradation, which includes methanogenesis, is inhibited. The TS and VS concentrations before and after the anaerobic digestion are shown in Figure 2.

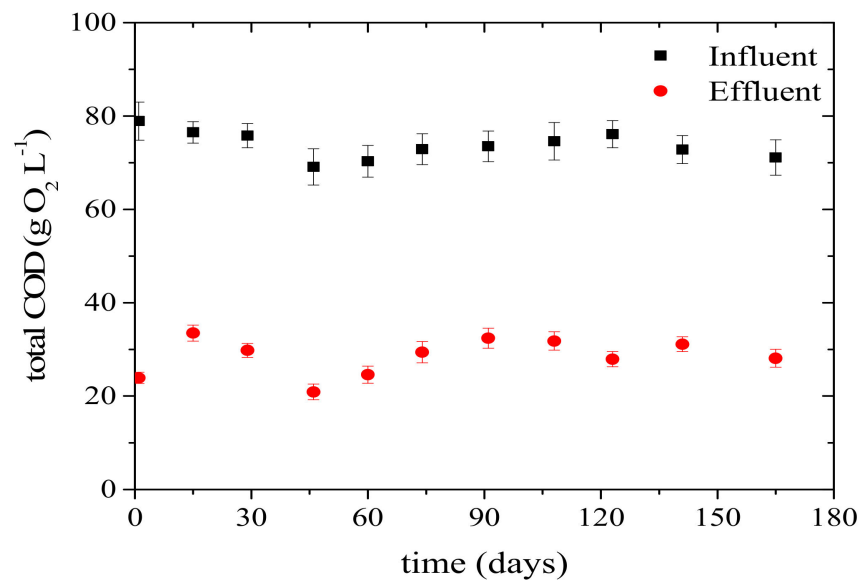


**Figure 2.** Average concentration of the TS and VS of the influent and the effluent of the anaerobic digestion treatment.

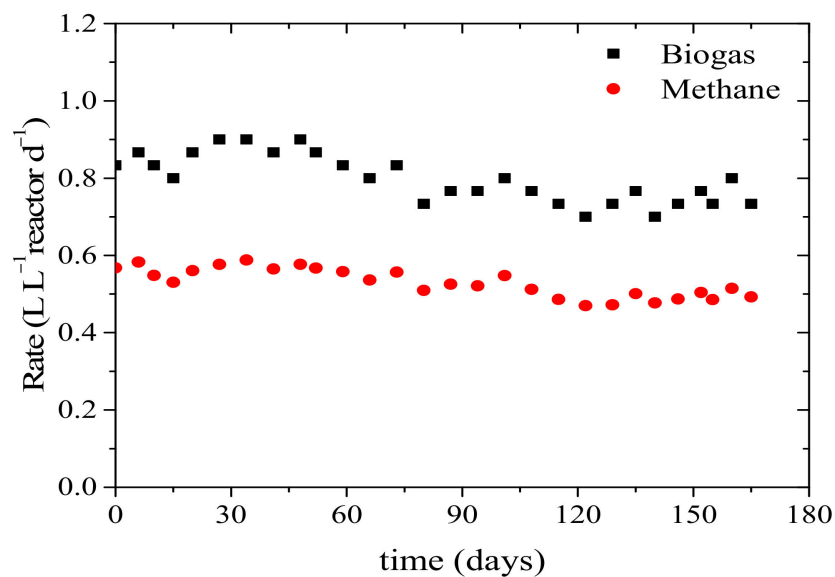
The concentration of TS in the influent of the reactor exhibited fluctuations, ranging between 45 to 60 gL<sup>-1</sup> due to variations in the starting waste sources, while the respective values in the effluent tended to stabilize without significant discrepancies ( $22.9 \pm 1.89$  g L<sup>-1</sup>). Respectively, the VS concentration in the influent and effluent of the CSTR followed the same trend as the TS, with starting average values of 34–51 gL<sup>-1</sup>, reduced to 12–19 g L<sup>-1</sup> after treatment. Moreover, after the first 74 days of operation, the system can be considered to be in equilibrium, after which an average TS removal of  $53.4\% \pm 5.3$  and an average VS removal of  $63.6\% \pm 6.2$  were observed. It is clear that the selected temperature of the reactor (40 °C) enhanced the hydrolysis of solids. The COD values of the waste mixture before and after the anaerobic digestion treatment are shown in Figure 3.

The profile of COD, a parameter that is closely related to the presence of organic compounds that can be oxidized, both at the inlet and outlet of the reactor, can be considered generally stable, while a significant reduction in the COD values after treatment was observed. On average, the percentage reduction during the last operational period of the reactor was found significant, quantified at  $59.9\% \pm 3.1$  (for the last experimental

period). Accordingly, Figure 4 represents the methane and biogas generation rate during the operational period of the CSTR.



**Figure 3.** Average total COD of the influent and the effluent of the anaerobic digestion treatment.

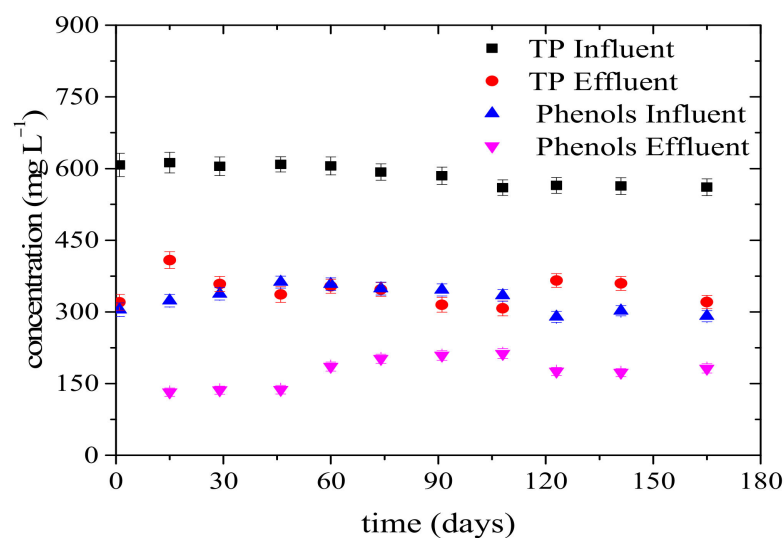


**Figure 4.** Average generation rate of biogas and methane during the anaerobic digestion treatment.

The production rates of biogas and methane during the operation of the CSTR were found to be very high and, especially for biogas, the average values ranged from 0.7 to 0.9 L per liter of reactor volume per day, while for methane the generated gas value was found to be 0.5–0.6 L per liter of reactor volume per day, respectively. The normalized biogas and methane production rate can be expressed in relation to the quantity of the volatile solids in the influent of the reactor, which are  $651.0 \pm 91.1 \text{ mL g}^{-1} \text{ VS}_{\text{added}}$  and  $433.8 \pm 58.2 \text{ mL g}^{-1} \text{ VS}_{\text{added}}$ , respectively. Similar results have been reported for the specific methane rate in other studies for mixtures containing food waste [24–26]. For example, food waste with pig manure resulted in a methane generation of  $388 \text{ mL g}^{-1} \text{ VS}_{\text{added}}$ , food and garden waste in  $490 \text{ mL g}^{-1} \text{ VS}_{\text{added}}$ , and food waste, goat manure, and cow manure in  $264 \text{ mL g}^{-1} \text{ VS}_{\text{added}}$ , respectively. The average composition of biogas in methane was almost 65%, a phenomenon that is in excellent agreement with the literature for similar types of waste [27].

The generation of these gases in an anaerobic digestion reactor is closely connected to the organic load of the treated waste and the degradation stages of the anaerobic digestion. Thus, for each g of COD that is reduced, 0.75 L of biogas is produced. The high biogas and methane production heavily depend on the concentration of organic compounds that are degraded during treatment, a parameter that can be linked to the high volatile solids and COD values of the treated waste in this study. Furthermore, the high gas production rates also indicate that the anaerobic degradation of the waste mixture included all stages of hydrolysis, acidogenesis, oxygenation, and methanogenesis, as both methane and carbon dioxide were produced as the final products.

Next, we monitored the concentration of TP and phenols both in the inlet and outlet of the CSTR. The respective results (Figure 5) clearly indicate a significant reduction in the TP concentration after the anaerobic digestion, due to the consumption of phosphorus by the microorganisms towards their metabolic activities.



**Figure 5.** Average concentration of total phosphorus and phenolic compounds (expressed as gallic acid) of the influent and effluent of the anaerobic digestion reactor.

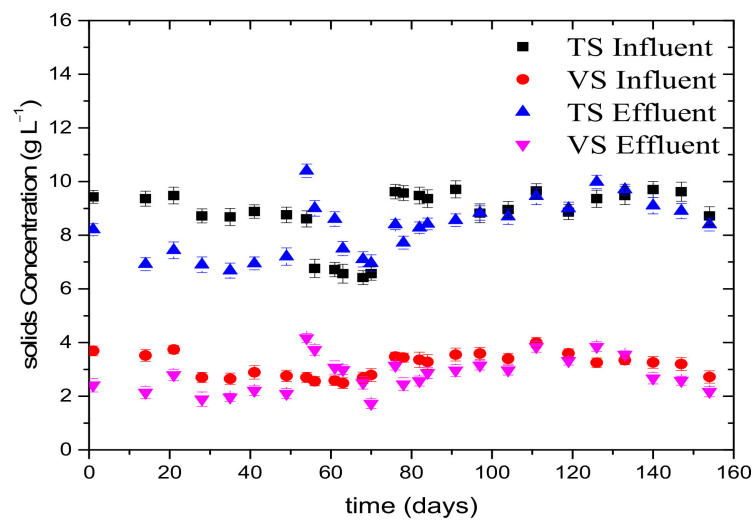
More specifically, after the 74th day of operation of the CSTR reactor when the equilibrium had been reached, the average removal of TP reached  $41.2\% \pm 3.9$ . The respective removal rate of the phenolic compounds (expressed as gallic acid) during treatment was found to be similar to the above results at  $40.9\% \pm 3.6$  after equilibration of the reactor.

### 3.2. Oxic–Anoxic Treatment

The anaerobic digestion of the waste mixture was followed by an oxic–anoxic treatment step and the most important physicochemical properties of the studied waste were again monitored. The pH values before and after the SBR step presented a slight decrease after the 60th day of operation. For example, after the first 91 days of operation where the system can be considered to have reached the equilibrium point, the effluent's pH values were quantified in the range of 6.3–6.6 compared with the respective values of 8.1–8.4 for the influent. The pH reduction can be assigned to the biological activity of the SBR microorganisms that consumed the organic content of the waste towards the generation of  $\text{CO}_2$ , which was then dissolved into water to produce  $\text{H}_2\text{CO}_3$ . The latter then generated  $\text{HCO}_3^-$ , followed by the in-turn production of  $\text{CO}_3^{2-}$  that increased the acidity of the SBR-treated waste. In addition, during the aerobic cycle of the SBR, the microorganisms oxidized ammonia to nitrite and then to nitrate, resulting in a decrease in the average pH values.

Next, the TS and VS concentrations in the inlet and outlet of the SBR were quantified and the respective results are shown in Figure 6.



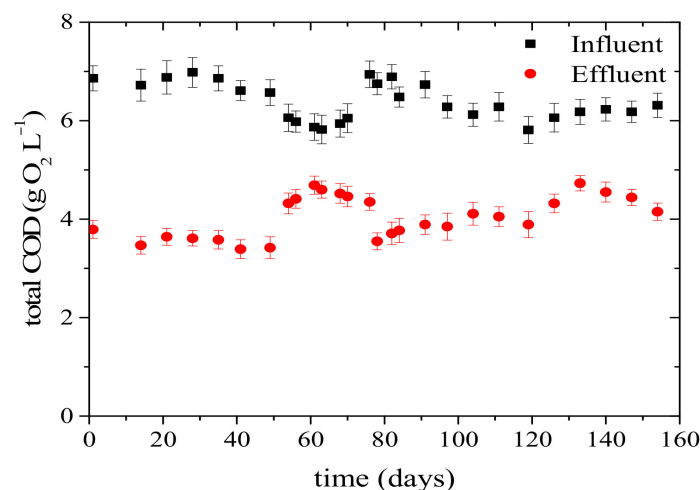


**Figure 6.** Average concentrations of the TS and VS of the influent and the effluent of the oxic–anoxic treatment.

Regarding the TS and VS concentrations during the operation of the SBR, three discrete regimes can be observed:

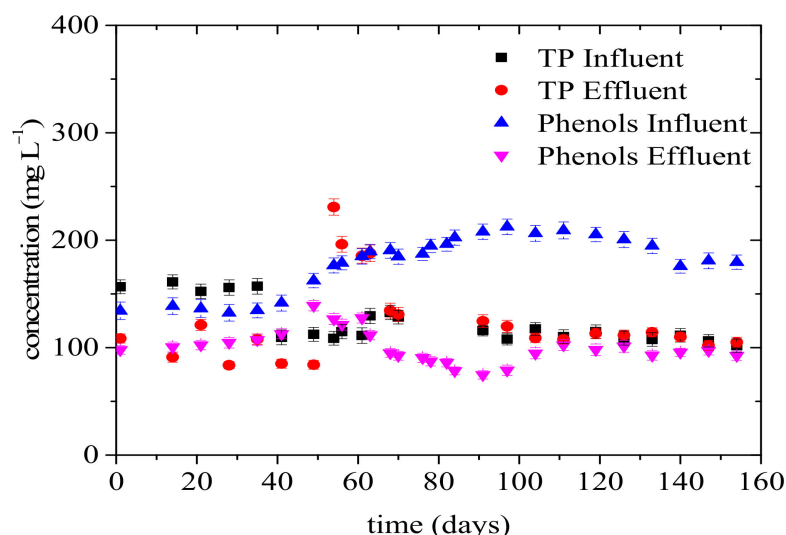
- From 0–49 days. For the first 49 days of operation, fluctuations of the average TS values were observed, while the values in the effluent were lower than those quantified in the influent of the SBR. The reason for the observed instability is the fact that the effluent of the previous CSTR step comprised the influent of the SBR, and these 49 days of the SBR operation correspond to the first operation period of the CSTR during which it had not reached equilibrium yet. In addition, during this period, solids dissolved into the mixture, while the biomass adhered to the walls and lid of the reactor.
- From 54–70 days. During this period, the adhered biomass was removed from the lid and walls of the SBR due to stress during the aeration of the mixture. As a result, the TS and VS values in the effluent of the reactor increased.
- From 91–154 days. After 91 days, the SBR has reached an equilibrium, during which the TS and VS concentrations in the influent and effluent of the reactor are comparable.

The COD values of the SBR-treated mixture were also found to decrease during the SBR treatment (Figure 7), with a more pronounced decrease during the first days of operation of the SBR, which corresponds to the lower content of TS in the effluent, as already mentioned above. The percentage reduction during the last 80 days of the operational period of the reactor reached  $\sim 33.2\% \pm 5.8$ .



**Figure 7.** Average total COD of the influent and the effluent of the SBR.

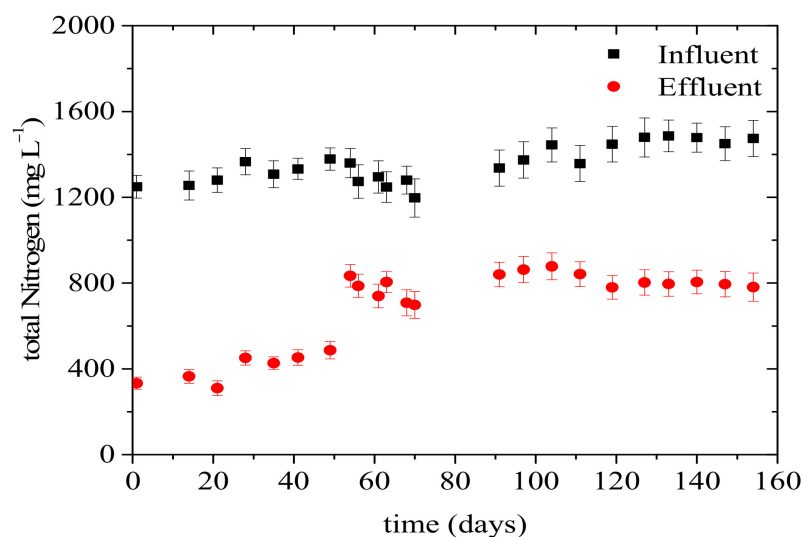
Next, the effect of the SBR treatment on the phenolic content of the waste mixture was investigated and the results are shown in Figure 8. A remarkable decrease in the phenols of the treated waste was observed after the 60th day of operation when compared with the respective values before the SBR treatment, while this decreasing trend tended to stabilize after the system had reached equilibrium. More specifically, the average removal of phenolic compounds was quantified  $53.4\% \pm 6.2$ , from  $197.7 \text{ mgL}^{-1}$  in the influent to  $91.5 \text{ mgL}^{-1}$  in the effluent of the SBR. Regarding the TP before and after the oxic–anoxic treatment, no significant decrease was observed, as phosphorus is mainly retained in the solids of the SBR according to the literature [28]. This comes in good accordance with the observed increase in the TP effluent concentration in the time period of day 54 to 63 (from  $84.1$  up to  $230.9 \text{ mg L}^{-1}$ ), for which an increase in the TS of the system (Figure 6) was also reported, due to the removal of biomass from the walls of the reactor. As a result of the increased presence of solids in the supernatant, which are mainly responsible for the removal of phosphorus as mentioned above, enhanced TP values were quantified in the aliquot that was collected for characterization during this time period.



**Figure 8.** Average phenolic compound (expressed as gallic acid) and total phosphorus concentrations of the influent and effluent of the SBR.

Furthermore, the effect of the oxic–anoxic treatment on the average concentration of the TN was evaluated. As can be seen in Figure 9 for TN, after equilibration of the SBR on day 91, a  $44.4\% \pm 3.3$  decrease in the TN concentration was quantified, from  $\sim 1428 \text{ mgL}^{-1}$  to  $\sim 795 \text{ mgL}^{-1}$ , in the influent and the effluent, respectively. Analysis for the determination of the concentration of inorganic forms of nitrogen (ammonium, nitrite and nitrate) in the last sample of influent and effluent of the SBR process was performed, and the concentration of ammonium nitrogen was found to decrease from  $550$  to  $110 \text{ mg L}^{-1}$ . On the other hand, the concentration of nitrite and nitrate nitrogen increased from  $3.9 \text{ mg L}^{-1}$  and  $13.9 \text{ mg L}^{-1}$  to  $297 \text{ mg L}^{-1}$  and  $112 \text{ mg L}^{-1}$ , respectively. These results indicate that nitrification and denitrification processes took place in the SBR during this experimental period. In our case, after the 70th day, a decrease in the nitrogen reduction rate was observed, which can be attributed to the biomass that was attached to the walls. This comes in agreement with the total solids concentration profile as demonstrated in Figure 7, in which after the 70th day influent and effluent were in equilibrium; therefore, no more biomass was further attached. On the contrary, in the first experimental period (until the 70th day) solids in the effluent were found less than in the influent, so more biomass was active until the biofilm was formed, which resulted in the deactivation of the inner layers. As far as nitrification is concerned, it is clear that a not complete conversion of ammonium nitrogen to  $\text{NO}_x$  took place, which can be associated with an inhibition of ammonium

and nitrite oxidizing bacteria. Svehla et al. reported a gradual increase in nitrite nitrogen concentration, which was accompanied by a decrease in nitrate nitrogen in a CSTR-treating liquid phase of digestate from an agricultural biogas plant, using pig slurry and grass silage. This behavior was attributed to the value of pH in the reactor which was not controlled and decreased throughout the experiment. Moreover, they performed the same experiment while controlling the pH (to the value of 7.0) and, in this case, the researchers did not observe any accumulation of nitrite nitrogen, a phenomenon that practically promotes the conversion of total ammonia nitrogen to nitrate [29].



**Figure 9.** Average concentration of TN of the influent and the effluent of the SBR.

Therefore, further study is needed in order to maximize the performance rates in the oxic–anoxic process, in which examination of critical parameters including the oxic–anoxic time, the pH and temperature values, and the solids retention time have to be evaluated. In the proposed process herein, this stage is merely used as a pretreatment of the digestate in order to further treat the produced waste with zeolite for a simultaneous recovery and valorization of nutrients.

### 3.3. Adsorption Experiments

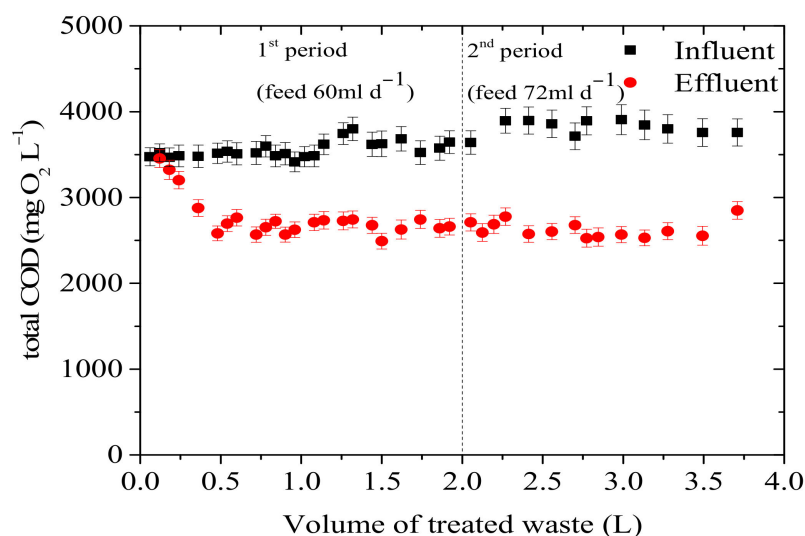
Next, the centrifuged SBR effluent was used as the influent for the following adsorption experiments. The first adsorption approach that was evaluated was, as already mentioned, the simple magnetic stirring of the waste with the zeolite of two granule sizes, and the most important physicochemical parameters monitored, before and after treatment, are shown in Table 3. It is clear that the value of pH decreased with an increasing zeolite quantity for all samples. Concerning the total phosphorus removal values, the adsorption on zeolite was found significant (exceeding 85%), while even for the sample with no stirring, the percentage removal was high, up to 50%. Similar behaviour was observed for the COD, which decreased from 3351 mg L<sup>-1</sup> to 1484 mg L<sup>-1</sup> for the 10 g (coarse) sample (55.7%). For the above two physicochemical parameters, the coarse zeolite exhibited an overall superior performance than its ground analogue. This was not the case for the adsorption of total nitrogen, that was also found to be dependent on the concentration of zeolite, but for which the ground type of zeolite presented better results when compared with the zeolite with a larger granule size. The stirring process and the concentration of the zeolite did not significantly influence the adsorption efficiency for phenols concentration. As a representative example, the phenols adsorption efficiency of 5 g coarse zeolite under stirring reached ~43.7% compared with a ~47.9% reduction for the 10 g coarse zeolite experiment under stirring and ~39.4% without stirring.

**Table 3.** Physicochemical parameters of the treated waste before and after zeolite treatment (in suspensions), using different zeolite quantities and granule sizes.

Parameter	Initial Sample	2 g		5 g		7 g		10 g		10 g, No Stirring	
		0–1 mm	1.5–3 mm	0–1 mm	1.5–3 mm	0–1 mm	1.5–3 mm	0–1 mm	1.5–3 mm	0–1 mm	1.5–3 mm
pH	8.25	7.9	8.3	8.2	8.3	8.0	8.2	8.1	7.9	7.8	7.6
COD (mg L <sup>-1</sup> )	3351	2103	1948	1780	1639	1736	1540	1641	1484	2596	2793
TP (mg L <sup>-1</sup> )	60	8.3	6.3	5.2	3.2	5.0	2.8	3.3	2.9	25.0	37.0
TN (mg L <sup>-1</sup> )	425	328	356	275	315	270	307	247	295	320	361
phenol (mg L <sup>-1</sup> )	71	42	44	41	40	39	39	38	37	40	43

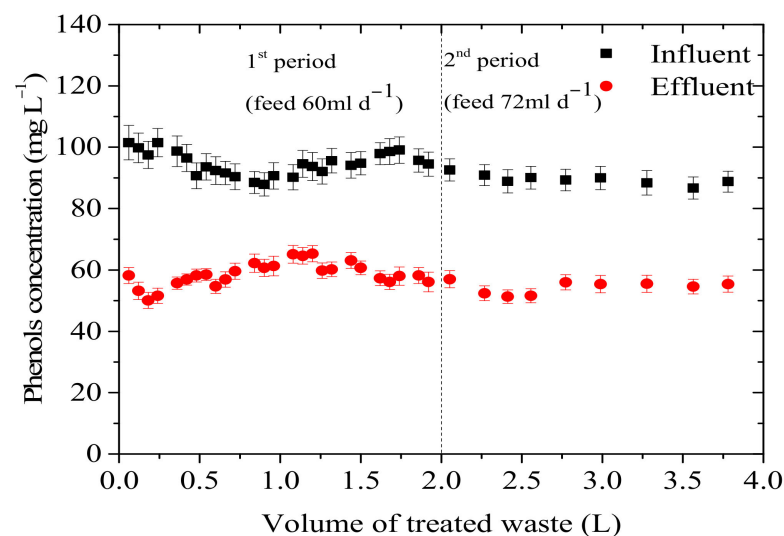
We have to highlight though that the ability of both types of zeolites to adsorb nutrients such as nitrogen and phosphorus that are found present in the tested waste indicate that such an approach can be successfully exploited for the recovery of nutrients for agricultural purposes. Similar results were presented by other researchers [30] who demonstrated that clinoptilolite was found to be a promising candidate for high removal efficiencies of nutrients (N, P, and K) by treating the liquid fraction of digestate from a centralized biogas plant in Denmark.

Next, column adsorption experiments were conducted, for which the waste feed was channeled continuously through the zeolite-packed column, following the aforementioned initial batch test in conical flasks. Figure 10 demonstrates the reduction profile of the COD before and after the adsorption column, with an observed COD decrease of  $31.9\% \pm 3.7$  for the 2nd experimental period. An increase in the waste feeding rate from 60 to 72 mL d<sup>-1</sup> was not found to affect the COD reduction at all.

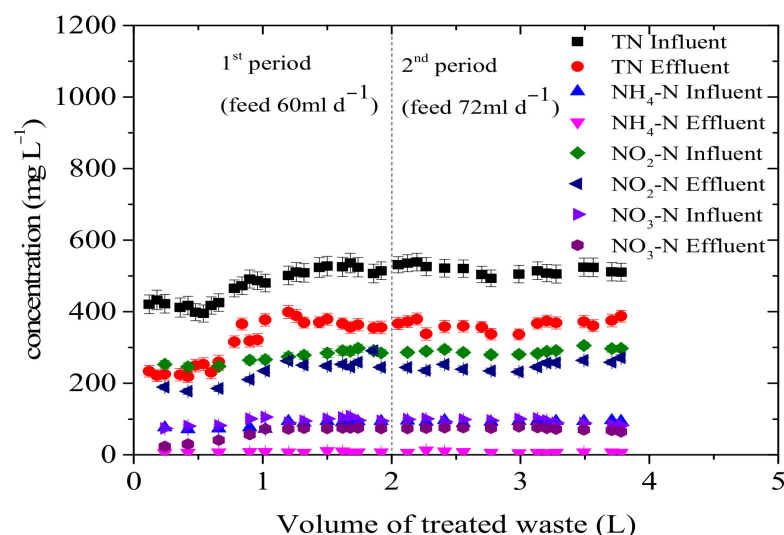
**Figure 10.** Average total COD of the influent and the effluent of the zeolite column.

Similar behaviour was observed for the phenolic concentration and total nitrogen values and the results are presented in Figures 11 and 12, respectively. The average removal efficiency reached  $39.4\% \pm 2.4$  and  $29.6\% \pm 3.0$ , respectively. Concerning phenols adsorption on zeolite, it has been reported that the Langmuir isotherm adequately described the uptake equilibrium, confirming that the monolayer adsorption capacity and the percentage of the removal were dependent on contact time, adsorbent dose, and initial phenol concentration [31]. High ammonium reduction was observed between the influent and effluent of the column, with a stable behavior and a percentage reduction of  $91.3\% \pm 1.7$  and  $92.4\% \pm 2.4$  for the two waste feed rates, respectively. The average ammonium concentration in the influent was  $89.2 \pm 8.2$  mg L<sup>-1</sup> and in the effluent  $7.2 \pm 1.9$  mg L<sup>-1</sup>. The adsorption capacity of NH<sub>4</sub><sup>+</sup> for Clinoptilolite-treated landfill leachate has been reported

with a value of 10.8 mg per g [17]. In a recent study [32], the results showed that Clinoptilolite demonstrated stoichiometric exchange between ammonium and potassium in urine solutions with mobile cations in the zeolite. Moreover, there have been many reports for the adsorption of low-concentration ammonium on zeolite, which can be attributed to a single-ion exchange process or electrostatic attraction [33,34]. Concerning the nitrate and nitrite nitrogen concentration in the effluent of the SBR (influent of zeolite column), it is obvious that the nitrite concentration is up to four times higher, which can be attributed to an inhibited or suppressed growth rate of nitrite-oxidizing bacteria (NOB). This is in agreement with a previous study, which reported that alternating oxic–anoxic conditions caused a lag phase in the NOB compared with ammonium-oxidizing bacteria [35].

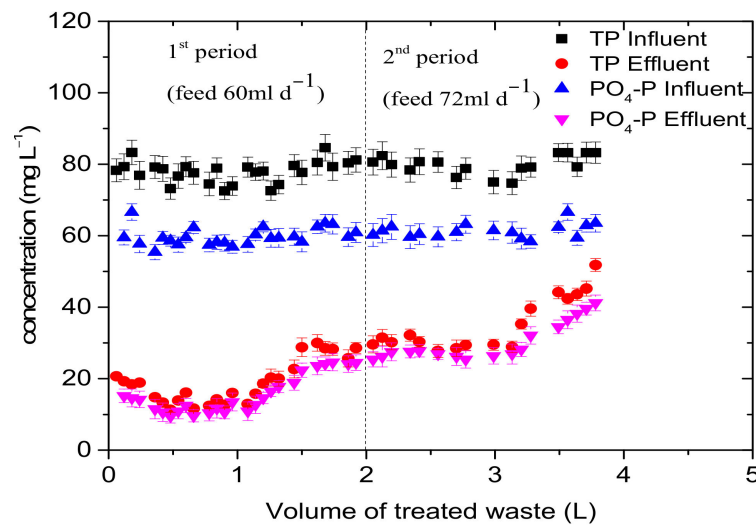


**Figure 11.** Average phenolic compound concentration (expressed as gallic acid) of the influent and effluent of the zeolite column.



**Figure 12.** Concentration of TN of the influent and the effluent of the zeolite column.

In contrast with our experimental observations for phenols and TN as mentioned above, total phosphorus adsorption was affected by the feeding rate, as can be observed in Figure 13, which strongly suggests that the available surface of zeolite for phosphorus compounds is limited. A mechanism for phosphorus removal has been proposed in the literature, in which calcium was the preferred desorbed cation.



**Figure 13.** Average TP of the influent and the effluent of the zeolite column.

Moreover, the increase in the initial ammonium concentration has been reported to enhance the phosphorus removal rate, while a shift in the value of pH from 8 to 9 resulted in a much faster and more efficient rate. On the other hand, ammonium sorption to zeolite was less efficient, due to the shifted  $\text{NH}_3/\text{NH}_4^+$  equilibrium [36]. Another study claimed that the natural Ca-loading of the applied zeolite may be responsible for not completing CaP-precipitation and P-loadings are limited by the available Ca-cations in the zeolite structure [37]. Cations concentrations were reported as critical parameters for the effective recovery of phosphate due to the formation and mineralogical type of precipitates [37]. Similar results have been reported by Wan et al. for treating sludge fermentation liquid with zeolite, demonstrating that the ammonium recovery relied on adsorption on zeolite through cation exchange, and the recovery of phosphate depended on precipitation with  $\text{Ca}^{2+}$  released from zeolite, which is related to the adsorption of ammonium on the zeolites [38].

The ability of digestate nutrient-enriched Clinoptilolite to supply nitrogen to plants as a fertilizer, as well as its superiority when compared with biochar has been already reported in previous works [39]. This highlights the potential exploitation of the natural zeolite used in the integrated approach for the treatment of complex mixtures of waste with high organic strength proposed herein as a high-added-value fertilizer. Overall, the integrated sequential treatment proposed in this work resulted in a significant remediation of the treated waste mixture. In Table 4, a comparison between the physicochemical characteristics of the waste mixture before (influent) and after (effluent) of the zeolite column treatment approach is presented.

An almost complete remediation of the treated waste is observed in this work, while these results are superior to those reported in the literature when a single treatment process is employed. In a recent study [40], zeolite was used for treating digestate from food waste, in order to enhance the composting process and was found responsible for 45% total nitrogen loss. Moreover, the addition of zeolite caused a significant loss in the ammonium nitrogen concentration due to adsorption (initial day of the experiment), which was dependent on the quantity of the zeolite. For example, 15% of zeolite resulted in the decrease in  $\text{NH}_4\text{-N}$  from  $4574 \text{ mg kg}^{-1} \text{ dm}^{-1}$  to  $3382 \text{ mg kg}^{-1} \text{ dm}^{-1}$ . In another representative work, when only zeolite adsorption was employed for the treatment of olive mill wastewater, Aly et al. reported a ~48% decrease in phosphorus [12]. Moreover, Kolakovic et al. observed a 50% COD and 70% TN reduction when employing zeolite for the treatment of dairy processing wastewater [41]. In the same direction, Kotoulas et al. observed only a 40% decrease in the organic load of cheese whey using zeolite-packed columns [5]. The results reported in this work highlight the importance of an integrated, sequential treatment approach for the efficient remediation of complex waste mixtures



towards the safer disposal of the final effluent and nutrient utilization by producing added-value products, such as biogas and bio-fertilizers.

**Table 4.** Physicochemical characteristics of the non-treated and final waste mixture.

Parameter	Value Before Treatment	Influent Zeolite Column	Effluent Zeolite Column	Zeolite Column% Average Removal	% Remediation (Overall Approach)
COD (g L <sup>-1</sup> )	71.08–76.14	3.63	2.71	25.3	96.3
TN (mg L <sup>-1</sup> )	1424–1778	490	333	32.0	79.2
NH <sub>4</sub> -N (mg L <sup>-1</sup> )	n.d.	89.2	7.2	91.9	-
NO <sub>2</sub> -N (mg L <sup>-1</sup> )	n.d.	282	242	14.2	-
NO <sub>3</sub> -N (mg L <sup>-1</sup> )	n.d.	94.1	67.6	28.2	-
TP (mg L <sup>-1</sup> )	560–593	78.7	25.4	67.7	95.6
PO <sub>4</sub> -P (mg L <sup>-1</sup> )	n.d.	60.4	21.6	64.2	-
Phenols (mg L <sup>-1</sup> )	281–349	93.4	57.5	38.4	81.7

n.d.: not determined.

#### 4. Conclusions

In this work, a sequential waste management approach was presented comprising a CSTR step, followed by SBR treatment, and last by adsorption processes using natural zeolite towards the efficient remediation of waste mixtures of complex nature and high organic strength. The following conclusions can be drawn:

- High biogas (0.7 to 0.9 L per liter of reactor volume per day) and methane (0.5–0.6 L per liter of reactor volume per day) production rates and high COD removal rates (~60%) were observed during the CSTR treatment step.
- The SBR treatment resulted in significant TN (~44%) and COD (~33%) reduction values compared with the influent values (effluent of the CSTR) during the last operational period of the reactor.
- Adsorption experiments with simple stirring of the zeolite and the waste were deemed efficient towards the removal of the pollutant indices under evaluation, with the coarse zeolite exhibiting a higher performance compared with its ground analogue.
- Column adsorption experiments with ground zeolite were inefficient due to the saturation of the column resulting in a short column lifetime. On the contrary, the coarse zeolite packed column exhibited an extended lifetime and an excellent performance towards COD removal (~32%) as well as phenol (~39%) and TN (~30%) retention compared with the influent values (effluent of the SBR), a behavior that was found independent on the waste feed rates. High retention efficiency was also observed for TP, but in this case, the performance of the column was suppressed upon an increase in the waste feed ratio.

In conclusion, high removal rates of all the important physicochemical parameters were observed in the final effluent of the proposed strategy, a phenomenon that signifies that the whole process can be environmentally friendly and economically viable by exploiting the byproducts. Zeolite can be further successfully utilized towards nutrients reuse for agro-industrial purposes. Additional research is recommended for optimizing the performance of the oxic–anoxic process, although the presented results are very promising. For the direct discharge of the treated waste and depending on the criteria applicable, the final effluent may require further treatment by ultrafiltration and/or reverse osmosis [1,42].

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