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Second Cheese Whey Treatment Using Zeolite under Continuous Flow Mode and Its Application on Wheat Growth

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Abstract: The efficiency of natural zeolite to treat second cheese whey (SCW) and remove ammonium from artificial wastewater (AWW) was examined. Since zeolite has been reported to improve nitrogen availability in soils, its effect on wheat plant growth was also examined. Continuing a previous study using batch reactors, results are presented concerning experiments in fixed-bed columns under continuous operation. Results from the continuous flow column experiments using AWW and zeolite (2.0–2.8 mm) indicated that low flow rates (4 mL/min and 8 mL/min) did not significantly affect zeolite adsorption ability, while maximum zeolite adsorption capacity reached 15.30 mg NH_4^+-N/g. Finally, the effect of zeolite saturated with NH_4^+-N on plant growth was examined. The application of saturated zeolite affected significantly wheat plant growth and resulted in faster growth and higher biomass production.

Keywords: zeolite; secondary cheese whey; ammonium removal; column experiments; continuous flow; plant growth experiments

1. Introduction

Due to their large volumes, high pollutant loads, and seasonality, agro-industrial wastewaters (e.g., from dairies, olive mills, and wineries) pose a serious environmental threat if released untreated [1,2]. Specifically, wastewaters from cheese industries (such as Second Cheese Whey—SCW) contain high concentrations of nutrients such as ammonium nitrogen (0.06–0.270 g/L) and total phosphorus (0.006–0.5 g/L) and high organic load (chemical oxygen demand (COD) and biological oxygen demand (BOD): 0.8–102.0 and 0.6–60.0 g/L, respectively) and suspended solids [3,4].

Although several technologies and processes have been tested to treat agro-industrial wastewaters, including biological systems, electrochemical methods, constructed wetlands, advanced oxidation processes, or hybrid systems including two or more of the above-mentioned methods [3,5,6], biological trickling filters and constructed wetlands (CWs) currently appear the most effective technologies due to their high dissolved COD (d-COD) degradation rates, which can reach up to 26.3 g d-COD/(L day) for biological trickling filters and 685.49 g d-COD/(m^2 day) for CWs [5,7,8]. On the other hand, circular economy principles express that wastewater treatment should be combined with simultaneous energy production and/or nutrient recovery. For this purpose, various zeolites (natural or modified) have been tested as low-cost absorbents to adsorb nutrients (i.e., nitrogen and phosphorus) from agro-industrial wastewater streams [9–15]. It should be mentioned that most previous research has examined the use of zeolite under batch mode and continuous flow experiments are limited [12,16–19]. Kolakovic et al. [13] examined the possibilities and effects of treating dairy wastewaters in laboratory-scale filter columns under continuous flow operation, however, were used adsorbents based on organo-zeolites and not on natural zeolite. They found that a fine-grained filter (with zeolite of diameter 1.45 mm) achieved maximum nitrate nitrogen (70%) and phosphate (20%) adsorption removal efficiencies.

Another important aspect of zeolite's use for wastewater nutrient recovery is its potential use as a soil amendment. Several studies have examined the effect of zeolite on the growth of various plant species. These experiments mostly concern the use of unsaturated zeolite, as a controlling agent, as it's water and nutrient release is slow in various plants (i.e., *Zea mays*, *Hordeum vulgare* L. seedlings, *Raphanus sativus*, rice, cucumber, *Aloe vera*, soybean cultivars, sugarcane, corn, sorghum, Leccino olive, and sunflowers) [20–39]. On the other hand, zeolite has been used as a bulking agent to produce compost derived from various wastes, such as sewage sludge [40], biogas digestate [41], and food waste [42].

Only a few studies [43–48] have examined the use of saturated zeolite as a potential fertilizer replacement, and these mainly used nutrient-rich aqueous solutions to saturate zeolite with nitrogen and phosphorus. For example, (a) saturated zeolite with phosphorus [43,45] that increased the growth of lettuce, tomato, rice, and *Andropogon* grass by 20%; (b) saturated zeolite with urea [44] that increased silage corn's dry-matter leaf production; (c) saturated zeolite with potassium nitrate [46] that increased lettuce yield; (d) saturated zeolite with ammonium and potassium [47] to increase spinach yield; and (e) zeolite enriched with cations in soilless cucumber cultures [48].

The purpose of this study was to examine the use of zeolite to treat second cheese whey (SCW) and artificial wastewater (AAW) in continuous flow column experiments. In addition, to examine the effect of saturated zeolite with ammonium originating from SCW and AWW on the growth of wheat plants (*Triticum* spp.) and its potential use as a fertilizing agent.

2. Materials and Methods

2.1. Materials

The artificial wastewater (AWW) used in the continuous flow column experiments was NH_4Cl aqueous solutions using deionized water (DW). NH_4Cl was dried at 104 °C for 24 h and then diluted to the desired concentration (the initial NH_4^+-N concentration of the AWW was 200 mg/L). The second cheese whey (SCW) used in this study was obtained from the Papathanasiou S.A. dairy (Agrinio, Greece), transported to the laboratory in plastic bottles, and then stored at −20 °C until use to prevent any change in its composition. The COD concentration of the undiluted SCW was 28.500 mg/L, total Kjeldahl nitrogen (TKN) was 243 mg/L, NH_4^+ was 45.27 mg/L, PO_4^{3-} was 196.69 mg/L, and its pH was 4.2 [15].

The natural zeolite used in the experiments, originated from Bulgaria (Imerys Minerals Bulgaria AD, imported by Zeolife ™ Company, Nea Orestiada, Greece), and is a hydrated aluminosilicate mineral of volcanic origin (clinoptilolite content: 85%; moisture content: 10–12%; impurities of feldspar, micas, and clays free of fibers and quartz: 3–5%). According to the technical data sheet provided, the minimum cation exchange capacity value of this specific zeolite is 150 meq/100 g. Prior to all experiments, the zeolite was sieved to obtain the desired granulometry (i.e., 2.0–2.8 mm), washed to remove dust, and finally dried [15].

2.2. Continuous Flow Column Experiments

Zeolite of granulometry 2.0–2.8 mm was used for the continuous flow column experiments to determine the zeolite's maximum adsorption capacity for ammonium. This specific granulometry was chosen based on previous experiments examining the efficiency of zeolite to remove ammonium from SCW and AWW under batch operating conditions [15]. The columns used for the experimental setup are described in Kotoulas et al. [15] and comprised Plexiglas tubes, 40.0 cm in height with a 4.0 cm internal diameter, equipped with four sampling valves placed at different heights (Figure 1). Each column was filled with 500 g of 2.0–2.8 mm zeolite. For experiments on AWW the flow rates of 4 and 8 mL/min were applied that correspond to hydraulic loading rates (HLR) of 4.43 m^3/m^2 day and 8.86 m^3/m^2 day, respectively. For experiments on SCW, the flow rates of 15 mL/min and 25 mL/min were applied that correspond to HLRs of 16.61 m^3/m^2 d and 27.69 m^3/m^2 day, respectively. Samples were collected at regular intervals from the upper sampling valve. The columns were fed with either AWW containing 200 mg NH_4^+-N/L or with SCW diluted with tap water to 50%. Ammonium concentration in AWW was chosen, in order to compare the results with previous batch experiments, while ammonium concentration in SCW experiments could not been regulated, due to SCW's unstable quality. Initially experiments have been performed using AWW with relatively high NH_4^+-N concentration (200 mg/L). The choice of HLRs (4 mL/min and 8 mL/min) has been made in order to achieve a desired contact time of the liquid with the zeolite avoiding operational problems during the process. However, for experiments using diluted SCW (diluted with water, presenting less initial NH_4^+-N concentration (28 mg/L or 9 mg/L) than AWW (200 mg/L)) increased flow rates, 15 mL/min and 25 mL/min (compared to those applied in AWW treatment) were used in the continuous flow column experiments to avoid prolonged experiments and biofilm formation.

Figure 1. The laboratory-scale continuous flow columns.

2.3. Plant Growth

To determine the effect of zeolite saturated with NH_4^+-N on plant growth experiments were carried out using wheat plants (*Triticum* spp.). Wheat was chosen due to its rapid growth and nitrogen fertilizing needs. The experimental procedure, which followed literature guidelines [49], included the following.

1. Preparation of NH_4^+-N saturated zeolite: 2 kg of zeolite was placed in an aqueous solution containing 5000 mg NH_4^+-N/L for two days. The mixture was then filtered under vacuum and the zeolite was washed with deionized water to remove any free ammonium ions from the surface of the zeolite particles and dried in an oven at 100 °C.
2. Determination of the weight of saturated zeolite to be added to each pot: Firstly, zeolite's NH_4^+-N content was calculated to determine the appropriate amounts of zeolite for each treatment (Table 1). Samples of zeolite were saturated with either aqueous ammonium solution or SCW. Following complete saturation, the adsorbed NH_4^+-N was calculated (i.e., 5.67 mg NH_4^+-N/g zeolite for aqueous ammonium solution and 0.235 mg NH_4^+-N/g zeolite for SCW). The treatments were carried out in triplicate (three pots) and while the experimental design was based on fully randomized blocks. Treatment Z-SCW (Table 1) refers to the use of zeolite also saturated with NH_4^+-N derived from SCW.
3. Pot preparation: 10 kg of sandy loam soil was placed in each pot. The soil had previously been dried in 80 °C and passed through a 5-mm sieve. Pot bottoms were fully closed to avoid nitrogen losses. Zeolite was added in soil's surface and afterwards six wheat seeds were planted in each container at a depth of 3 cm and 2–3 cm apart.
4. Plant growth: Soil pH (previous to zeolite addition) was 6.35, while irrigation was performed according to the prevailing climatic conditions and based on the water capacity of the sandy loam soil (i.e., 18%). The pots received sufficient daylight for plant growth and room temperature was 19–24 °C.
5. Plant biomass harvest: The wheat plants were maintained in suitable growth (Figure 2) conditions for 75 days. On day 75, all plants were harvested, measured, and their wet and dry masses calculated.
6. Statistical analysis: A one-way between groups analysis of variance (ANOVA) at the 95% significance level was used to examine the effect of different zeolite treatments on plant growth. Post hoc pair comparisons were also performed to test equal variations using Tukey's honestly significant difference test. Homogeneity of variance tests (Levene) were bypassed since the number of data points for each group was the same. Statistical analyses were performed using SPSS Statistics 23.0 for Windows.

Table 1. Zeolite treatments.

Pot Code	Desired NH_4^+-N Content (mg/kg) of Pot Soil	Weight of Zeolite Added to Each Pot (g)
Z0	0	0.00
Z1	10	17.63
Z2	20	35.26
Z3	30	52.89
Z4	40	70.53
Z5	50	88.16
Z6	60	105.79
Z-SCW	10	426.31

2.4. Analytical Methods

Total ammonium concentration was measured using the salicylate test as initially described by Verdouw et al. [50] with modifications [15], where in 1 mL of sample 0.25 mL of hypoclorite solution and 0.25 mL of the salicylate/catalyst solution are added. The sample is left for 5 to 10 min to develop a blue color and then the absorbance at 625 nm is measured using a spectrophotometer. The pH and EC of the soil samples were measured in aqueous extract (using 1:10 *w*/*v*) using a multiparameter meter (HANNA HI5521, Hanna Instruments, Woonsocket, Rhode Island, U.S.A.). Total Kjeldahl nitrogen (TKN) in the soil samples was measured following Bremner and Mulvaney [51], TKN in water samples was measured using the titrimetric method according to Standard Methods [52]. All the reagents used in this study were of analytical grade.

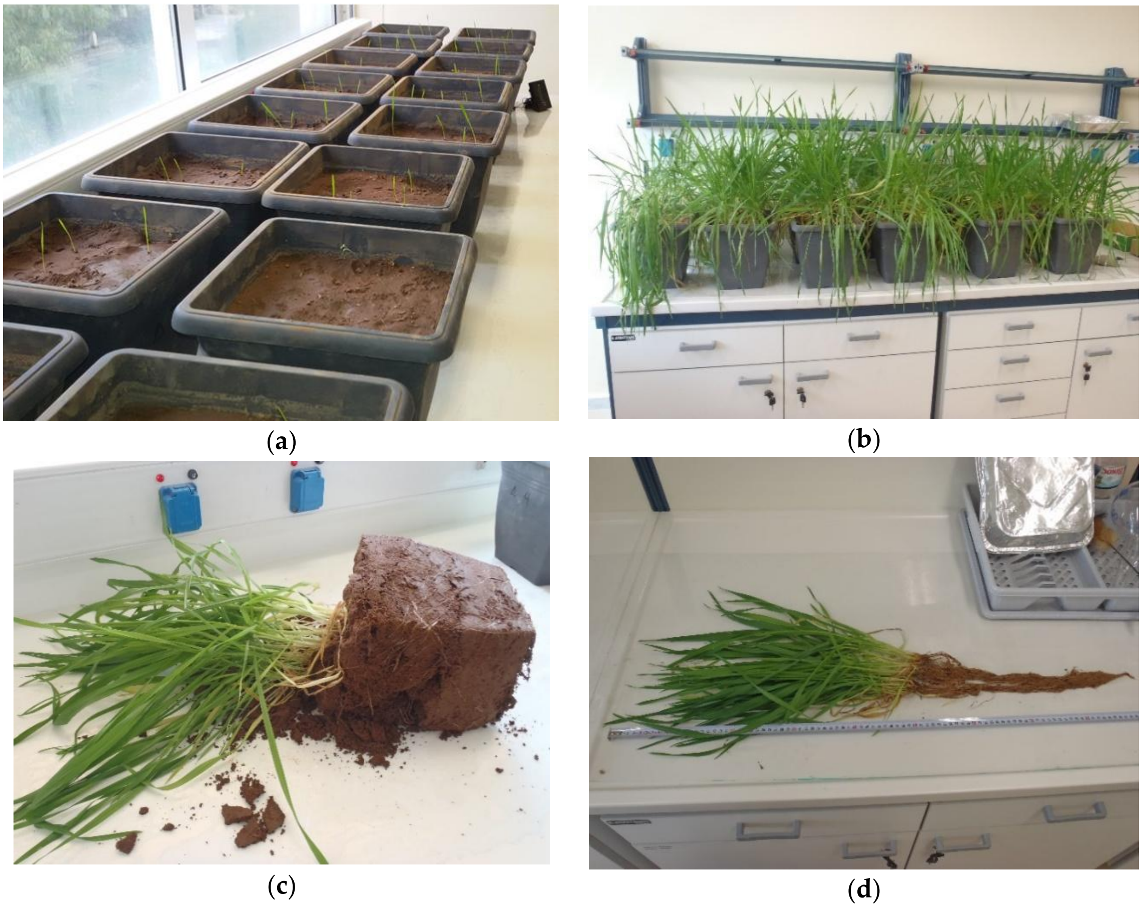
(**a**) (**b**) (**c**) (**d**)

Figure 2. Wheat plants (**a**) eight days after seed planting, (**b**) 75 days after seed planting, (**c**) following harvesting, and (**d**) following soil removal.

3. Results and Discussion

3.1. Adsorption Experiments in Continuous Flow Laboratory-Scale Columns Using AWW

Initially, experiments were performed using artificial wastewater (AWW). Figure 3 presents the time series charts of NH_4^+-N concentrations in column effluents for two different flow rates (i.e., 4 mL/min and 8 mL/min). The initial NH_4^+-N concentration of the AWW was 200 mg/L, while column void volume was 380 mL. Zeolite proved to be rather efficient at adsorbing NH_4^+-N, as NH_4^+-N concentrations remained below 1 mg/L after 4560 min and 2000 min treatment time for the flow rates 4 mL/min and 8 mL/min, respectively. These flow rates correspond to approximately 45 bed volumes of treated AWW.

Zeolite became completely saturated after 16,000 min and 9600 min treatment time for the flow rates 4 mL/min and 8 mL/min, respectively, which correspond to approximately 168 bed and 202 bed volumes of treated AWW. Nevertheless, the crucial value of NH_4^+-N effluent concentration is 15 mg N/L, i.e., the legislation limit for treated wastewater [53]. The time points at which NH_4^+-N concentration in column effluent reached this limit was 6240 min for the flow rate of 4 mL/min, and 2900 min for the flow rate of 8 mL/min, corresponding to approximately 65 bed volumes of treated AWW.

The effect of flow velocity on zeolite adsorption capacity in the laboratory-scale filter was insignificant. At 4 mL/min, maximum zeolite adsorption capacity was recorded as 14.68 mg NH_4^+-N/g after 16,080 min of operation, while for a flow rate of 8 mL/min, maximum adsorption capacity was 15.30 mg NH_4^+-N/g after 9610 min of operation. Therefore, increasing the flow rate slightly increased the ability of the specific zeolite to bind with NH_4^+-N, thus reducing the required treatment time. Moreover, comparing previous batch [15] and continuous flow column experiments with flow rates of 4 mL/min and 8 mL/min, it is clear that in batch experiments with initial NH_4^+-N concentration of 200 mg/L, the zeolite adsorbed 0.152 mg NH_4^+-N/g after 1440 min [15], while in the continuous flow experiments the total amount of adsorbed NH_4^+-N was two orders of magnitude higher (15.30 mg NH_4^+-N/g).

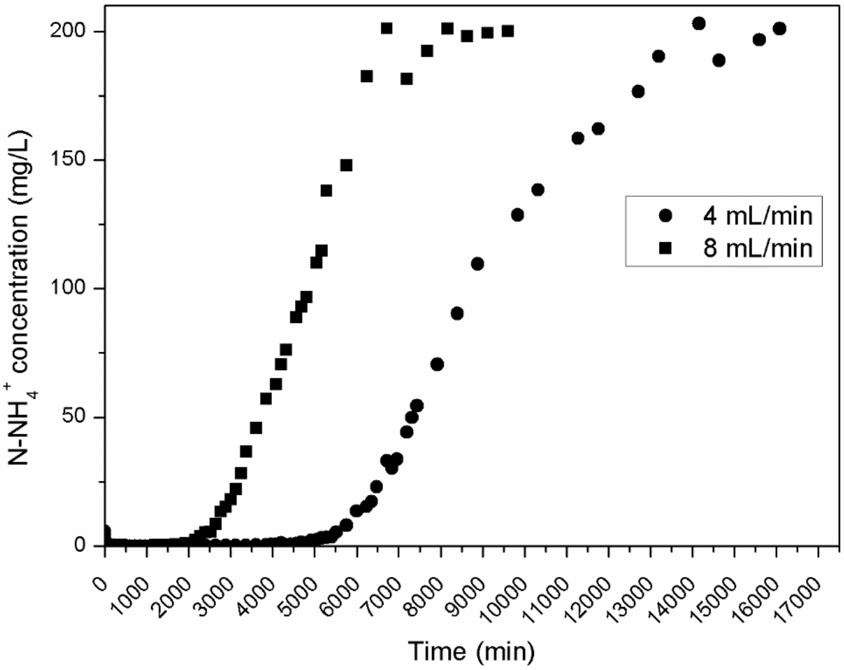

Figure 3. NH_4^+-N concentrations in effluent from columns fed with artificial wastewater (AAW).

Second cheese whey (SCW) is a high-strength wastewater as it contains significant amounts of NH_4^+-N, total phosphorus, and organic substances [3,4]. Therefore, it could be used as a source of recovered nutrients. Since flow rate did not affect adsorption capacity for AWW, increased flow rates of 15 mL/min and 25 mL/min (compared to those applied in AWW treatment) were used in the continuous flow column experiments, along with a 50% dilution of SCW to avoid prolonged experiments and biofilm formation and retain ammonium load to comparable values as in the AWW case.

Figure 4 presents the time series charts of NH_4^+-N concentrations recorded in column effluent for both flow rates when columns were fed with 50% SCW. The initial concentrations of NH_4^+-N in the SCW were 28 mg/L and 9 mg/L for the 15 mL/min and 25 mL/min flow rates, respectively (since SCW were obtained in different seasons and at different times of the day, presenting different characteristics), and column void volume was 380 mL. Although no plateau is presented in Figure 4, zeolite was considered saturated, when the NH_4^+-N effluent concentrations were the same with feeding convention.

In these experiments the zeolite became completely saturated after 690 min and 330 min for the flow rates of 15 mL/min and 25 mL/min, respectively, and this corresponds to approximately 27 bed and 22 bed volumes of SCW, respectively. Maximum adsorption capacity of the zeolite was recorded as 0.36 mg NH_4^+-N/g (for 15 mL/min flow rate) and 0.08 mg NH_4^+-N/g (for 25 mL/min flow rate). After 520 min treatment time, the NH_4^+-N effluent concentration in the column with 15 mL/min flow rate, exceeded 15 mg N/L, which is the legislation limit for treated wastewater [53]. This corresponds to approximately 21 bed volumes. In experiments where the 25 mL/min flow rate was applied, the NH_4^+-N concentration recorded in the effluent remained constantly below 15 mg N/L. This is because the NH_4^+-N influent concentration was below 15 mg N/L. This significant difference in ammonium adsorbance capacity between experiments using artificial (15.30 mg NH_4^+-N/g) and real wastewaters

(0.36 mg NH_4^+-N/g), has also been reported in previous studies [11] and is attributed to the competitive behavior of several ions for available adsorption sites on the zeolite for nitrogen removal. In order to prolong zeolite's service life in full-scale experiments and avoid ion competition, a proper pretreatment should be applied, which will remove the major part of the organic load (e.g., biological trickling filter) [5].

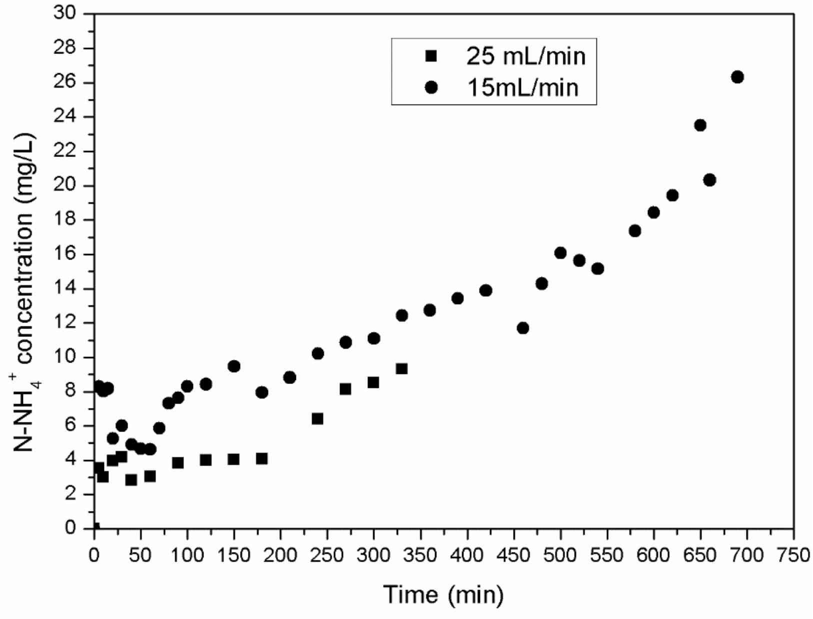

Figure 4. NH_4^+-N concentrations in effluent from columns fed with 50% second cheese whey (SCW).

In both columns, COD removal was recorded as approximately 21%, which is consistent with the findings of previous experiments [15]. These relatively low COD removal rates are attributed to zeolite saturation, as biological COD removal is limited because biofilm growth is minimal during the first three days of the experiment [15]. In full-scale applications SCW should be treated prior to the zeolite's filter, to reduce organic load below legislation limits, using various treatment methods (e.g., biological trickling filters and constructed wetlands) [5,8]. Ortho-phosphate PO_4^{3-} P removal rates were also low for both columns, approximately 29%, due to the zeolite's limited ability to adsorb PO_4^{3-} P.

3.2. *Effect of Zeolite on Plant Growth*

The zeolite used in this study has a high cation-exchange capacity, and thus can improve soil cation-exchange capacity and enhance the availability of elements around plant roots. This property promoted an investigation on reusing the saturated zeolite as a fertilizer substitute in the frame of a circular economy [54,55]. In zeolite, N binds to the negative exchange station and is released at a suitable time for absorption by plants, which can lead to an increase in biomass yield. For this purpose various amounts of saturated zeolite were used to fertilize wheat (*Triticum* spp.) seeds. Wet and dry weight of the biomass and shoot lengths were measured and presented in Table 2.

Table 2. Average values of wet and dry mass and plant length per treatment.

Pot Code	Wet Mass (g)	Dry Mass (g)	Shoot Length (cm)
Z0	9.62 ± 1.09	1.57 ± 0.03	48.65 ± 1.01
Z1	13.69 ± 1.12	2.06 ± 0.05	51.11 ± 0.98
Z2	15.56 ± 2.09	2.20 ± 0.01	52.19 ± 1.23
Z3	15.23 ± 1.98	2.11 ± 0.02	53.96 ± 1.52
Z4	16.74 ± 1.57	2.14 ± 0.04	50.72 ± 0.89
Z5	14.37 ± 1.34	2.33 ± 0.08	54.44 ± 1.32

Z6	14.31 ± 1.21	2.25 ± 0.06	51.64 ± 1.09
Z-SCW	14.99 ± 1.18	2.09 ± 0.02	52.23 ± 1.08

Results of the physicochemical characteristics of the zeolite enriched soils are shown in Table 3. Although soil pH values were not significantly affected by the added zeolite, soil EC values did increase from 60.35 mS/cm to 99.80 mS/cm. This attributed to the ability of zeolite to retain cations and release them at the expense of salts [22].

Table 3. Physicochemical characteristics of zeolite enriched soils.

Pot Code	pH	Electrical Conductivity (mS/cm)	Total Kjeldahl Nitrogen (TKN) (%)
Sandy loam soil	6.35	60.35	0.1120
Z0	6.59	97.35	0.0840
Z1	6.88	98.33	0.0280
Z2	6.69	81.53	0.0197
Z3	6.62	81.50	0.0560
Z4	6.63	94.97	0.0187
Z5	6.67	99.80	0.0181
Z6	6.57	91.63	0.0193
Z-SCW	6.71	89.67	0.0179

The use of ammonium saturated zeolite positively influenced wheat growth, as plant mass and length were higher in the zeolite enhanced treatment pots. To examine if the differences in plant dry mass and length between the different treatments were statistically different, ANOVA analysis was performed. The ANOVA *p*-values (Table 4) indicate that the use of ammonium saturated zeolite significantly affected wheat plant dry mass (*p*-values < 0.05). On the other hand, the amount of zeolite added to each treatment pot did not significantly affect plant dry mass. Additionally, plant length significantly increased ($p < 0.05$) only when the high amount of zeolite (Z4, Z5, and Z6) was added to the soil. This could imply that the amounts of zeolite used in these experiments were not adequate to significantly increase the growth of wheat plants, especially considering that the amounts of nitrogen amount added to the pots ranged from 1 kg/ha to 6 kg/ha when the recommended amount for wheat is 125 kg/ha [56]. The addition of larger amounts of saturated zeolite was not possible due to the spatial confines of the small, laboratory-scale experiments and to previous suggested zeolite masses per kg of soil in previous related studies [43–46].

Table 4. ANOVA *p*-values for dry mass and plant length comparisons.

Treatment Comparison	*p*-Values for Dry Weight	*p*-Values for Plant Length
Z0–Z1	0.063	0.325
Z0–Z2	0.026	0.337
Z0–Z3	0.036	0.038
Z0–Z4	0.028	0.005
Z0–Z5	0.002	0.012
Z0–Z6	0.037	0.017
Z0–Z-SCW	0.015	0.228
Z1–Z2	0.529	0.693
Z2–Z3	0.69	0.51
Z3–Z4	0.911	0.154
Z4–Z5	0.267	0.003
Z5–Z6	0.721	0.025
Z2–Z-SCW	0.897	0.75

4. Conclusions

In this study, natural Bulgarian zeolite was investigated for its effectiveness to remove ammonium from artificial wastewater (AWW) and to treat second cheese whey (SCW) in continuous flow column experiments, while saturated zeolite was used to examine its effect on the growth of wheat plants (*Triticum* spp.). The conclusions reached from this study are as follows.

- Continuous flow experiments with AWW and SCW indicate that zeolite could effectively adsorb absorb NH_4^+-N up to 202 bed volumes before its complete saturation. Nevertheless, the use of SCW reduces NH_4^+-N, as several ions compete with NH_4^+-N in zeolite's absorbance.
- Different flow rates did not greatly affect zeolite adsorption ability, as maximum adsorption capacity was 14.68 mg NH_4^+-N/g for the flow rate of 4 mL/min and 15.30 mg NH_4^+-Ng for the rate of 8 mL/min.
- SCW should be treated using other methods before introduced in a zeolite filter, to decrease organic load and to prolong zeolite's service life.
- Saturated zeolite positively influenced wheat plant growth, as the dry mass of plants grown in soils treated with zeolite was significantly higher than that of plants grown in soils without zeolite treatment.

SCW and other agro-industrial wastewaters contain high nitrogen loads, which should be recovered and reused for agricultural purposes. The present study proves that zeolite could retain a significant portion of nitrogen load from SCW, which can serve as a fertilizing agent. Thus, agro-industrial wastewaters treatment using zeolite can not only reduce pollutant loads, but also recover significant portions of nutrients, which can be further reused.

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