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EVALUATION OF THE REMOVAL EFFICIENCY OF AMMONIUM AND SOME HEAVY METALS FROM AGRICULTURAL WASTEWATER ON THE ZEOLITIC SUBSTRATE OF AN EXPERIMENTAL WASTEWATER TREATMENT PLANT

This study is intended to evaluate the adsorptive potential of clinoptilolite zeolite, used as a filter medium in an experimental wastewater treatment plant for agricultural interests. Samples of technological water and wastewater from agricultural households and microfarms in Transylvania were analyzed, before and after filtration using natural zeolite from Rupea (ZNR) and Turbidex. The tests included the determination of pH, electrical conductivity, ammonium, and some heavy metals (Fe, Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb) for the characterization of the technological water/wastewater and the zeolite removal efficiency. The evolution of pH had an increasing trend, due to the alkalinity of the zeolite material, with similar values (7.2–7.4) before and after filtration of both water and with larger oscillations for wastewater (6.0–9.4). Electrical conductivity values decreased after both water (from 848 to 492 μS/cm) and wastewater (from 1277 to 933 μS/cm) filtration, correlating with increased alkalinity. The filtration media had a good adsorptive potential, with ZNR values being slightly higher than those of Turbidex's for NH_4^+ (88.02% and 86.85%, respectively) and ranked differently for heavy metals: Zn (72.45%) > Fe (66.45%) > Cu (43.76%) > Mn (43.69%) and Fe (67.41%) > Mn (65.65%) > Zn (60.84%) > Cu (56.08%), respectively.

1. INTRODUCTION

In the context of the continuous increase in clean water scarcity, over one billion people currently lack access to drinking water, and more than one-third of the global population lives in areas at high risk of water resource depletion [1, 2]. Agricultural

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activities, alongside industrial and domestic activities, significantly contribute to surface water pollution through the direct or indirect discharge of insufficiently treated or untreated wastewater. The reduction of freshwater sources is increasingly affecting many European regions, leading to major changes that gradually resemble the conditions in the Middle East [2].

In such areas, the recovery and treatment of wastewater using internal systems and devices for re-utilization in industrial processes at the level of agricultural households or microfarms would be a viable solution. Internal treatment procedures can also be applied to water from certain local sources intended for technological use in facilities that lack access to the public potable water supply network [3–5]. Natural zeolites have proven to be efficient adsorbent materials for the depollution of various water categories, with their potential for removing ammonium, iron, and heavy metals from water being well-known and widely accepted [6–10].

Current research provides abundant data on the use of modified zeolites in various fields, among which we highlight the efficiency of zeolitic nanocomposites in treating water polluted with heavy metals, dyes, and emerging pollutants [8–11]. Cationic granular zeolite, primarily indicated for the catalytic adsorption of heavy metals, is currently among the most recognized filtering materials, alongside quartz sand, metallurgical coke, marble, gravel, and diatomaceous earth [11, 12]. The diversification of filtering media has led to the continuous improvement of devices and systems for filtering both freshwater and wastewater. Among these, systems with zeolitic substrates are increasingly valued for water treatment through prefiltration or filtration processes [12]. Natural zeolites, along with metallurgical coke, can also be used in catalytic prefiltration, particularly for water polluted with iron and manganese, while substrates with marble or calcined dolomite yield good results for water with low or very low hardness and high CO_2 content [13]. Devices for prefiltering wastewater in agro-food technologies should combine the retention of suspended solid particles with procedures for pH and electrical conductivity correction, as well as gas removal (via aeration) or even minimal biological treatment (anaerobic, with antifoaming agents, urea, or soda) [12, 13]. Among the various types of filtering devices available, the current study uses pressure filters, which are recommended for treating high-flow water, as their high filtration speed significantly reduces the surface area of the filtering substrate [14–16]. Pressure filters with activated carbon or zeolite are suitable for treating various water categories, effectively removing color, odor, and excess chlorine. Zeolites and other ion-exchange substances serve as adsorbent substrates for cationic filters, where ion exchange occurs between their ions and those of the solution they encounter [13–16]. Zeolites, being crystalline aluminosilicates, form an effective catalytic filtering medium capable of reversibly losing or gaining water, which facilitates cation exchange without significant structural changes.

The compensation cations, being weakly bound, are easily replaced by cations from the solution, granting zeolites their ion-exchange properties [15]. Among natural zeolites frequently used in water treatment for the removal of heavy metals and other pollutants, clinoptilolite, mordenite, and chabazite have demonstrated particularly notable results [16–18]. Regarding the adsorption rate of clinoptilolite for heavy metals and ammonium, extensive data is available, revealing high efficiency, up to the complete retention of NH_4^+ [17–19]. This study aimed to evaluate the efficiency of some natural zeolites in removing ammonium and some heavy metals from technological water/wastewater, originating from commercial microfarms and traditional agricultural households, by using a wastewater treatment plant for internal reuse.

2. MATERIALS AND METHODS

2.1. ORIGIN AND COLLECTION OF THE INVESTIGATED WATER SAMPLES

The study included 3 commercial microfarms and 9 traditional agricultural households located in the Someșul Mare basin (Cluj and Bistrița-Năsăud counties), which discharge wastewater into surface waters or onto adjacent lands.

Table 1

The identification of the water/wastewater samples and the characterization of the source units

Sample	Type of farm	Technological dominants
[I /Tw]	microfarm	young cattle fattening facility with a septic tank
[II /Tw]		swine fattening facility without a septic tank
[III/Tw]		dairy sheep farm without a septic tank
[IV/Tw]	farmstead	mixed – swine and poultry with manure platform
[V/Tw]		mixed – lactating cows and swine with a manure platform
[VI/w]		mixed – lactating cows and swine with a manure platform
[VII/Ww]	microfarm	young cattle fattening facility with a septic tank
[VIII/Ww]		swine fattening facility without a septic tank
[IX/Ww]		dairy sheep farm, without a septic tank
[X/Ww]	farmstead	mixed – swine and poultry with manure platform
[XI/Ww]		mixed – lactating cows and swine with a manure platform
[XII/Ww]		mixed – lactating cows and swine with a manure platform
[XIII/Ww]	farmstead	mixed – swine and poultry without manure platform
[XIV/Ww]		mixed – lactating cows, with dairy facility and manure platform
[XV/Ww]		mixed – swine without manure platform
[XVI/Ww]		mixed – lactating cows with dairy facility and manure platform
[XVII/Ww]		mixed – lactating cows, with dairy facility and manure platform
[XVIII/Ww]		mixed – swine and poultry without manure platform

Tw – technological water, Ww – wastewater.

From these sources, 6 samples of technological water (predominantly surface water from controlled local sources) and 12 samples of wastewater were collected, the identification of which is shown in Table 1, along with the main characteristics of the investigated units.

2.2. ADSORBENT ZEOLITIC MATERIAL

Natural zeolite from Rupea (ZNR). The mineralogical characteristics of ZNR, along with its physicochemical properties and the tests conducted to determine these, are presented in the product's technical data sheet, with some aspects summarized in Table 2. Additional details are documented by the manufacturer and in various studies in the field [12, 15–19]. The selection of ZNR as the adsorbent substrate for the experimental station was also because it is a natural, low-cost material, easy to regenerate, and reusable as a soil amendment after depletion [15, 19].

Table 2

The main physicochemical and mineralogical characteristics of ZNR [17, 19]

Physical characteristics		Chemical composition [%]		Mineralogical composition [%]	
Softening point, °C	1250	SiO_{2}-	68.75–71.3	clinoptilolite	87–90
Melting point, °C	1320	Fe_2-O_3	1.90–2.1	plagioclase	2–5
Melting temperature, °C	1400	Al_2-O_3	11.35–13.1	anhydrite	2–3
Color	grey-green	MgO	1.18–1.20	cristobalite	4–5
Smell	odorless	CaO	2.86–5.2		
Porosity, %	32–44	Na_2-O	0.82–1.30		
Porous diameter, nm	0.4–0.6	K_2-O	3.17–3.40		
Hardness – Mohs scale	3.5–4.0	Loss on ignition	8.75–8.86		
pH	8.75				
Block density, tone/m^3	2.377				

Initially, three samples of natural zeolite from the quarries of S.C. Zeolites Production in Rupea were evaluated, representing commercial series differentiated by grain size: 0.5–1.5, 1.5–3, and 3–5. For the laboratory investigations, a primary preparation of the zeolite samples was done using a simple procedure recommended by the Zeolites Group and certain studies on ZNR [17, 19]. This procedure involved washing the zeolite with distilled water until the water remained clear, followed by drying at 105°C, cooling, and storage in a desiccator.

The investigations began with determining the methylene blue retention capacity of the three ZNR variants using the well-known column filtration model [20, 21]. Preliminary test results on the zeolite samples identified the ZNR variant with a grain size of 0.5–1.5 mm as having the highest adsorptive efficiency, supporting its selection as the adsorbent substrate for the experimental water treatment plant. This medium-grain zeolite allowed the formation of a sorbent bed suitable for the dimensions of the tank used (volume, cylindrical shape, diameter) and enabled high-flow water filtration with minimal pressure loss. The mineralogical and physicochemical characteristics of the investigated zeolitic material provide the filtering substrate with durable and efficient sorbent properties, ensuring a long operational lifespan of up to 2 years [16–19].

Turbidex filtering medium. Turbidex (commercialized by Also Business Invest) is primarily composed of clinoptilolitic zeolite with a medium grain size (0.6–1.4 mm), mixed with small amounts (0.1%) of quartz/silica. Turbidex is a next-generation zeolitic medium widely used in the United States, with a filtration efficiency comparable to current adsorbents [22]. It exhibits exceptional physical and ion-exchange properties, with its efficiency being dependent on the formation of a filtering bed appropriately matched to the tank's diameter and height.

2.3. IMPLEMENTATION OF THE EXPERIMENTAL WASTEWATER TREATMENT PLANT

The schematic representation of the experimental station is detailed in Figure 1, which is centered around a zeolite filter (model 1054ZT with Turbidex – MSDS-2013).

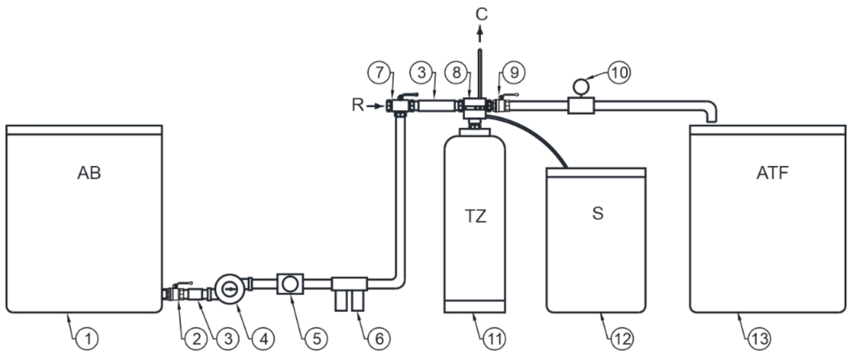

Fig. 1. The general blueprint for the experimental water treatment plant:
1 – raw water recipient tank (AB), 2 – faucet FI-FE Dn, 3 – flexible connection, 4 – pump,
5 – electro-pressure switch, 6 – filter, 7 – three – way valve Dn, 8 – electro valve,
9 – faucet FI-FE Dn, 10 – water meter, 11 – zeolite tank (TZ), 12 – brine tank (S),
13 – filtered water tank (ATF), R – water network, C – sewer discharge

The system is equipped with an inlet pump, an external drain, and an outlet for sample collection. The water flow is generated by a hydro pump that transfers water from the first tank (1 – AB) to the second tank (13 – ATF). These tanks have a capacity of 200 dm^3 each, ensuring the collection and homogenization of a significant volume of water samples. Through an electro valve, the filtration tower was connected to the public drinking water supply, the sewage system, and a brine tank for washing and regenerating the station. The station has the following technical specifications: a filtering bed with a height of 760–1200 mm (40 dm^3 of zeolite), an operating pressure of 0.3 MPa, and a flow rate of 1 m^3/h. When replacing the zeolitic substrate, the procedure recommended for assembling and disassembling the filter components and loading the zeolite tank was followed. During the filtration of the samples, a protocol was adopted that involved collecting at least two representative samples for analysis–one before and one after filtration–for each water sample. The filtration process included the following steps: sample preparation – the water sample was prepared by combining and homogenizing it in tank 1 of the station, followed by collecting the initial sample. The filtration cycle programming: a manual filtration cycle was programmed, and the hydro pump was activated. The final representative sample was collected from the outlet tank after the filtration process was completed, this being an average sample from the total volume of 200 dm^3 of filtrate. After each filtration cycle, the regeneration function was activated. This included processes such as mixing, loosening, brine regeneration, and washing the filtering substrate with water from the public supply.

2.4. THE ANALYSIS OF WATER SAMPLES

The water samples were organized into the following three experimental models, with the variables being technological water and wastewater [10], as well as the type of filtering medium: technological water – ZNR (A), wastewater – ZNR (B), and wastewater – Turbidex (C). Thus, the grouped water samples were transported to the laboratory and stored in a refrigerator (at 4 °C) before investigation.

Table 3

Tested parameters and the methods used

Parameter	Method and equipment
pH	pH/conductometer, SevenCompact Duo
EC, μS/cm	pH/conductometer, SevenCompact Duo
NH_4^+, mg/dm^3	SR ISO 7150-1: 2001. *Determination of ammonium. Manual spectrometric method*
Fe, mg/dm^3	SR EN ISO 11885: 2009. *Determination of selected elements by inductively coupled plasma optical emission spectroscopy (ICP-OES)*
Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, mg/dm^3	to a 20 cm^3 sample, 4 cm^3 of concentrated nitric acid were added. The mixture was boiled and diluted with ultrapure water. The samples were analysed using ICP-OES. The values were corrected using a coefficient of 1.25, determined by the dilution factor.

Laboratory analyses included two sets of investigations. The first set, aimed to characterize the technological water and wastewater samples, involved the evaluation of pH and electrical conductivity (μS/cm) using a pH/conductometer (SevenCompact Duo model). The second set was focused on the assessment of the adsorptive potential of zeolitic substrates, based on the adsorption rate of ammonium and certain heavy metals. For this purpose, the concentrations (mg/dm^3) of ammonium and iron were determined using standardized methods [23, 24], while the concentrations of heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb) were measured using inductively coupled plasma optical emission spectrometry (ICP-OES). Table 3 presents the tested parameters and the methods used, alongside the national standards for wastewater [25]. The obtained data were grouped according to the experimental variants and subjected to primary processing, including recording in correlative tables and illustration in suggestive graphs.

The collected data was consolidated and graphically processed using advanced computational tools (GraphPad, Microsoft Excel, Origin Pro) and subsequently subjected to descriptive statistical analysis to determine the mean, maximum value, minimum value, and standard deviation. The adsorptive potential of the zeolitic substrate was evaluated by calculating the removal efficiency of ammonium and heavy metals, using the following established formula for this calculation (initially adopted for calculating the removal efficiency of methylene blue) [17]:

$$R = \frac{C_i - C_f}{C_i} \times 100\%$$

where: C_i – initial concentration of pollutant, C_f – final concentration of pollutant.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF THE WATER SAMPLES

pH and electrical conductivity measurements enabled a concise characterization of the technological water and wastewater samples in the context of available tests for monitoring the quality of surface water in agricultural households. The pH evaluation revealed very similar average values before and after filtration for technological water (7.29 and 7.44, respectively) and large fluctuations in the case of wastewater samples (6.0–9.4). The distribution of these values, as shown in Table 4, indicates a clear trend of water alkalinization after filtration, which can be attributed to the increased pH of the zeolitic material. It is also worth noting that the pH of agricultural-use water should ideally range around 7.5–8, without deviating beyond the limits (6.5–8.5) specified in WHO guidelines [26].

The evolution of electrical conductivity (*EC*) was characterized by a consistent decrease in recorded values, both in the case of technological water (from 848 to 492 μS/cm) and wastewater (from 1277 to 933 μS/cm). According to the data presented in Table 4, the evolution of this parameter correlates with the increase in the alkalinity of the filtered water, this fact being attributed to the increase in bicarbonate content and/or the reduction in the concentration of dissolved minerals.

Table 4

Descriptive statistical values for pH and electrical conductivity

Parameter	Model	Mean		Maximum		Minimum		Standard deviation		Reference value
		RW	FTW	RW	FTW	RW	FTW	RW	FTW	
pH	A	7.29	7.44	7.72	7.85	6.70	7.12	0.34	0.25	6.5–8.5
	B	7.32	7.79	7.84	8.10	6.58	7.55	0.41	0.22	
	C	6.85	7.34	7.20	7.83	6.31	6.61	0.41	0.49	
EC, μS/cm	A	848	492.5	1009	720	719	137	96.68	203.46	2500
	B	1277.3	1110	1524	1320	925	808	251.79	207.25	
	C	1025	933.3	1253	1117	908	824	175.10	138.57	

RW – raw water, FTW – filtered water. Reference values for drinking water and wastewater [25, 28]

EC values are highly dependent on water temperature and are correlated with its mineralization degree, with wastewater discharges significantly influencing this parameter in natural water bodies [27]. A deficient sewage system can lead to increased *EC* levels in water due to the discharge of chlorides, phosphates, or nitrates. Most of the water samples investigated in this study belong to the category of surface water. Since there are no specific legislative norms regulating *EC* for surface water, the standards for potable water are commonly applied [28].

3.2. ANALYSIS OF THE CONCENTRATION AND REMOVAL EFFICIENCY OF AMMONIUM

Ammonium concentrations detected in most raw process water samples exceeded the regulated limits for drinking water, the limits according to the wastewater standards for all wastewater samples (Table 5). Thus, the average values decreased from 4.08±0.95 mg/dm^3 to 0.51±0.06 mg/dm^3 after process water filtration, the NH_4^+ removal efficiency by ZNR reaching 87.5%. Post-filtration, significant reductions have been recorded, with values dropping to 3.74±2.86 mg/dm^3 and 4.78±3.40 mg/dm^3, respectively, though these values still did not fall within the maximum permissible limits for wastewater. Based on the differences between these values, the NH_4^+ removal efficiencies were quantified at 88.54% for ZNR and 86.85% for Turbidex, respectively (Table 5). According to research, zeolites demonstrate exceptional efficiency in ammonium adsorption. In this regard, we highlight the findings of Alikış [29], who, after investigating a type of clinoptilolite from Turkey, observed the complete removal of NH_4^+ from water and an 82% reduction in suspended solids.

These results led to the recommendation of clinoptilolite as an alternative for upgrading multifunctional filters and even wastewater treatment plants. The efficiency of clinoptilolite in ammonium adsorption, due to its excellent ion-exchange capacity, has been demonstrated since the 1970s. This discovery has opened a field of significant interest for future research, which has focused predominantly on the use of clinoptilolite in the denitrification of various categories of wastewater [15, 17].

Table 5

Descriptive statistical parameters [mg/dm^3] and removal efficiencies of ammonium

Model	Mean		Maximum		Minimum		Standard deviation		*R* [%]	MAC	
	RW	FTW	RW	FTW	RW	FTW	RW	FTW		Dw	Ww
A	4.08	0.51	5.20	0.50	3.00	0.026	0.95	0.06	87.50	1.5	2.0
B	32.65	3.74	54.5	9.40	9.72	1.65	20.60	2.86	88.54		
C	36.37	4.78	48.0	9.80	19.0	0.12	10.13	3.40	86.85		

RW – raw water, FTW – filtered water, Dw – drinking water, Ww – wastewater, *R* – removal efficiency, MAC – maximum admissible concentration [25, 28].

3.3. ANALYSIS OF CONCENTRATION AND REMOVAL EFFICIENCY OF HEAVY METALS

Among the heavy metals analyzed in the water samples, only four (Mn, Cu, Zn, and Fe) exhibited spectrometrically detectable concentrations (Table 6).

Table 6

Descriptive statistical parameters values [mg/dm^3] and the removal efficiency of heavy metals

Parameter	Model	Mean		Maximum		Minimum		Standard deviation		*R* [%]	MAC	
		RW	FWT	RW	FTW	RW	FTW	RW	FTW		Dw	Ww
Mn	A	0.062	0.04	0.10	0.053	0.032	0.012	0.031	0.016	35.48	0.05	1.0
	B	0.235	0.113	0.50	0.50	0.055	0.032	0.200	0.189	51.91		
	C	0.099	0.034	0.15	0.045	0.048	0.012	0.041	0.008	65.65		
Cu	A	0.174	0.099	0.496	0.154	0.020	0.053	0.166	0.037	43.10	2.0	0.1
	B	0.201	0.109	0.496	0.125	0.115	0.078	0.145	0.016	44.43		
	C	0.485	0.213	0.743	0.286	0.180	0.085	0.235	0.074	56.08		
Zn	A	0.112	0.027	0.196	0.045	0.067	0.019	0.045	0.009	75.89	0.5	0.5
	B	0.074	0.028	0.116	0.058	0.026	0.014	0.032	0.016	69.02		
	C	0.166	0.065	0.290	0.171	0.040	0.025	0.118	0.056	60.84		
Fe	A	0.79	0.288	1.049	0.496	0.405	0.058	0.259	0.169	63.54	0.2	5
	B	2.285	0.70	4.79	1.41	0.90	0.41	1.650	0.38	69.36		
	C	0.62	0.202	0.94	0.34	0.34	0.062	0.21	0.09	67.41		

RW – raw water, FTW – filtered water, Dw – drink water, Ww – wastewater, *R* – removal efficiency, MAC – maximum admissible concentration [25, 28].

Manganese presented variable concentrations and removal efficiency across the three experimental models. Thus, for technological water, the recorded values were below the permitted limits for wastewater (1 mg/dm^3), both before (0.062±0.031 mg/dm^3) and after filtration (0.04±0.016 mg/dm^3), the removal efficiency level of ZNR reaching 35.48%. Referring to the drinking water standards(0.05 mg/dm^3), only one exceedance was observed, reaching 0.1 mg/dm^3 in the water sample from the microfarm I. In comparison, manganese concentration registered increased values in wastewater, frequently exceeding the accepted limits for wastewater upon discharge (1 mg/dm^3). In the wastewater samples from the two experimental models, Mn concentrations reached 0.235±0.20 and 0.099±0.041 mg/dm^3 before filtration. These values subsequently registered a decrease to 0.113±0.189 mg/dm^3 after filtration through ZNR and to 0.034±0.008 mg/dm^3 after filtration through Turbidex. The differences between the average values recorded before and after wastewater filtration indicated a slightly lower Mn retention rate for ZNR (35.48–51.91%) compared to Turbidex (65.65%) under filtration conditions involving pressure.

Copper presented an analogous behavior across the three experimental models, with the values recorded before and after filtration on the two zeolitic substrates being comparatively close. The total copper concentrations measured were close to the values indicated in the national legislative standard (0.1 mg/dm^3), with some minor exceedances recorded, but remaining below the maximum limit established for drinking water (2 mg/dm^3), according to WHO guidelines (Table 6). In circumstances of technological water, Cu concentrations were 0.174±0.166 mg/dm^3 before filtration, decreasing to 0.099±0.037 mg/dm^3 after filtration, resulting in a removal efficiency of 43.1%. Significant trends were also observed in the analysis of wastewater samples, where Cu concentrations more frequently exceeded the permissible limits for wastewater upon discharge. Before filtration, the recorded values were 0.201±0.145 and 0.485±0.074 mg/dm^3, respectively. After filtration, the concentrations decreased to 0.109±0.016 for ZNR and 0.213±0.235 mg/dm^3 for Turbidex. Even though the copper content in wastewater decreased significantly after filtration, its evolution was characterized by slight and frequent exceedances of the permissible limits for wastewater (0.1 mg/dm^3), but not of the WHO-regulated values (2 mg/dm^3). The overall results obtained across the three experimental models revealed high copper removal efficiency for both ZNR (43.1–44.43%) and Turbidex (56.08%), supporting the potential use of zeolite-based filters in the treatment of certain categories of technological water and wastewater.

The zinc levels showed minor differences in relation to the investigated water sources and categories (Table 6). The average values recorded before and after filtration of the two water categories on ZNR and Turbidex substrates were close to the national legislative standard for drinking water (0.5 mg/dm^3) and significantly below the levels recommended by the WHO (1 mg/dm^3). In the case of technological water, Zn concentrations reached 0.112±0.045 mg/dm^3 before filtration and 0.027±0.009 mg/dm^3 after filtration, with a removal efficiency of 75.89% for ZNR. Similar trends were observed for wastewater, where exceedances of national standards were insignificant and negligible. In these cases, higher values were recorded, with similar trends, revealing a few minor exceedances of the permissible limits.

The values recorded for wastewater in the two experimental models were 0.074±0.016 and 0.166±0.118 mg/dm^3 before filtration, decreasing after filtration on ZNR to 0.028±0.032 mg/dm^3 and on Turbidex to 0.065±0.056 mg/dm^3 (Table 6). The wastewater filtration process led to a slight decrease in Zn concentrations, which exceeded the permissible limits in only two households but remained within the WHO regulations [26]. The evolution of Zn removal efficiency revealed higher proportions for ZNR (69.02 –75.89%) compared to Turbidex (60.84%).

Iron concentrations in the technological water were 0.79±0.259 mg/dm^3, exceeding the limits set by national legislation [28] and WHO guidelines [26] for drinking water (0.2 mg/dm^3, Table 6). After water filtration on the ZNR substrate, Fe concentrations decreased to 0.288±0.169 mg/dm^3, indicating a very high removal efficiency (63.54%). For wastewater samples, iron concentrations increased slightly, reaching 2.285±1.65 and 0.62±0.09 mg/dm^3 before filtration. After the filtration process, the concentrations diminished significantly, reaching 0.70±0.38 mg/dm^3 for the ZNR substrate and 0.202±0.21 mg/dm^3 for the Turbidex substrate (Table 6). The overall analysis of the recorded values for this parameter did not reveal exceedances of the maximum allowable limits for wastewater discharging to water bodies (5 mg/dm^3). Additionally, the iron removal efficiency of the two zeolitic materials was quantified, with ZNR achieving values of 63.54% for clean water and 69.36% for wastewater, while Turbidex recorded values of 67.41% (Table 6). The comparative analysis of the values recorded for this parameter across the two filtering media indicated that both ensure high levels of water de-ironing, with very similar performance trends. It was also concluded that the two zeolitic materials can be effective in deferrization of various categories of water, including those of agro-food interest, and are suitable for filters operating under pressures comparable to those in public water supply networks.

3.4. ANALYSIS OF THE ADSORBENT POTENTIAL OF THE FILTERING MEDIA

The set of the resulting data obtained from evaluating the adsorption potential of the investigated filtering media revealed high retention rates for ammonium and heavy metals, both from technological water and wastewater. As shown in Fig. 2, the adsorption rate reached its highest level in the case of ammonium ions, with very similar values for the two filtering media exceeding 87%. This was followed by the group of metals, for which significant retention rates were recorded, ranging between 43 and 72%. The hierarchy of of average values of removal efficiency differed slightly between the two zeolitic media: Zn (72.45%) > Fe (66.45%) > Cu (43.76%) > Mn (43.69%) for ZNR, and Fe (67.41%) > Mn (65.65%) > Zn (60.84%) > Cu (56.08%) for Turbidex. Among the relevant research that supports the current study, that which primarily refers to the use of clinoptilolite in the treatment of certain water categoriesis noteworthy. Thus, among the investigations regarding the purification potential of ZNR, the studies conducted by Senilă et al. [17] in experimentally marked water samples stand out, evaluating a 98% removal efficiency for NH_4^+, as well as the following distribution of removal efficiences for heavy metals: Mn > Cd > Cr > Zn > Fe > Ni > Co > Cu > Ba > Pb > Sr [17]. High relevance is also attributed to the results presented by Abed et al. [15], who evaluated the ammonium removal capacity of ZNR in the range of 10.4–12.3 mg/g from synthetic solutions at 20°C and pH 6.09. The relevant research conducted on the zeolitic adsorption of zinc [17, 30] showed similar trends to those recorded in the present study. Bedelean et al. [30] reported that the high adsorptive efficiency of certain volcanic tuffs from northwestern Romania in wastewater treatment was primarily due to the increased adsorption rate of Zn. However, great relevance is given to the results provided by the manufacturer regarding the evaluation of ZNR's efficiency in water treatment.

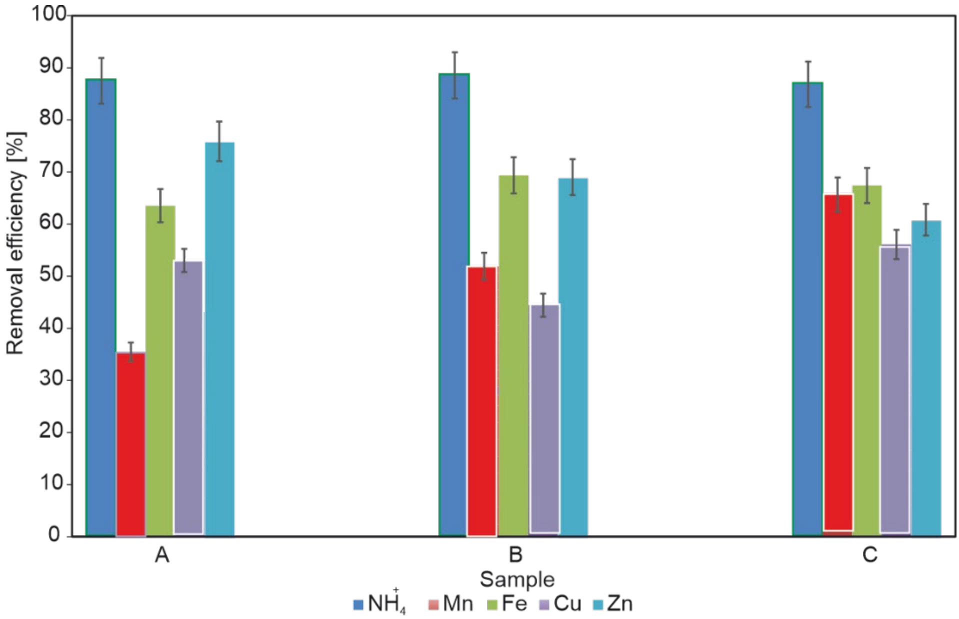

Fig. 2. Removal effficiencies of ammonium and heavy metals in the experimental models: technological water – ZNR (A), wastewater – ZNR (B), and wastewater – Turbidex (C).

The deterioration of surface water quality caused by nitrates, ammonium, and other pollutants originating from agricultural activities currently represents a major risk for agricultural areas [30–32]. These risks are monitored and mitigated by European and national legislation, which has implemented a set of key measures across Romania to reduce nutrient emissions [17]. The results of our study, corroborated with those of other researchers regarding the potential of ZNR to remove some metals (Pb, Cd, Cr and Cu), as well as an excellent ion exchange capacity [4, 12, 19], reveal that the treatment of technological water/wastewater with natural zeolites can be a technically and economically feasible solution for small units in the agricultural sector. Our results support the opportunity to use zeolitic devices and systems for wastewater treatment, enabling its recovery and reuse for irrigating various crops. These include food crops (for raw or processed consumption) or non-food crops (pastures and fodder, fiber crops, ornamental plants, seed crops, energy crops, or turf), as regulated by current legislation [31, 32].

4. CONCLUSIONS

The present study, based on the evaluation of the management situation of technological water and wastewater from several small agricultural units, as well as the implementation of a station for the experimental treatment of water of agricultural interest, enabled a comparative investigation of these water categories before and after filtration using natural zeolite from Rupea (ZNR) and Turbidex. The filtration process determined the increase of pH due to the alkalinity of the zeolitic medium, with similar values observed for technological water (7.2–7.4) and wider fluctuations for wastewater (6.0–9.4). Electrical conductivity values decreased from 848 to 492 μS/cm for technological water and from 1277 to 933 μS/cm for wastewater, correlating with increased alkalinity.

The experimental evaluation of natural zeolite from Rupea (ZNR) and Turbidex as filtration media for the treatment of technological water and wastewater from small agricultural units revealed distinct adsorption efficiencies for key parameters.

ZNR showed superior performance in the removal of ammonium (NH_4^+) and zinc (Zn), with retention rates of 88.02% and 72.45%, respectively. In contrast, Turbidex outperformed ZNR in retaining copper (Cu) and manganese (Mn), achieving removal efficiencies of 56.08% and 65.65%, respectively. For iron (Fe), both materials exhibited good removal capacity, with slightly higher efficiency observed for Turbidex (67.41%) compared to ZNR (63.54%). In all cases, the filtration process improved water quality by reducing electrical conductivity, increasing pH, and lowering contaminant concentrations.

Both ZNR and Turbidex demonstrated strong potential for the purification of agricultural wastewater, with each medium being more effective for specific target contaminants. Their complementary behavior suggests the possibility of using them in combination or in a staged treatment system to maximize overall removal efficiency.

Future perspectives include the optimization of filter configurations using sequential or hybrid systems, long-term testing under continuous flow conditions, and the development of scalable treatment modules suitable for integration into microfarms or household-level agricultural units. These steps would support the internal reuse of treated water, contributing to sustainable resource management in rural and semi-rural areas.

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