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REVIEW ARTICLE

Current aspects regarding the ecological impact of some wastewater recycling procedures and of zeolitic adsorption mechanisms

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Due to their specific properties, such as the ability to conduct ion exchange, their big internal surface, and their highly porous structure, natural and synthetic zeolites alike are successfully used to attach and remove heavy metals (Cd, Cr, Cs, Cu, Fe, Hg, Mn, Ni, Pb, Sr, W, Zn) and ions (ammonium) from wastewaters, industrial residues, contaminated soils, and industrial sludge. These volcanic tuffs are also excellent sorbent environments for permeable reactive barriers and systems used to decontaminate wastewater. This review includes an ensemble of relevant scientific studies regarding the analysis of the treatment and recycling of wastewater and heavy metal contaminated soils, with specific reference to the use of zeolites from Rupea and Baia-Mare. The compositional analysis of the zeolites revealed insignificant variations of SiO_2 (56.85-59.31%), Al_2O_3 (11.94-12.88%), and a Si/Al ratio 4 times bigger, which is specific to clinoptilolite, as opposed to the ratio that is usually found in the structure of other zeolites. Other major constituents that were identified in the chemical structure of clinoptilolite are CaO (2.67-2.83%), K_2O (2.30-2.40%), and Fe_2O_3 (1.24-1.59%), MgO (1.42-1.62%). Compositionally, the zeolite from Baia-Mare is very similar to the clinoptilolite from Rupea. Based on data resulting from the treatment of heavy metal contaminated soil (Cd, Cr, Cu, Pb, Zn) with clinoptilolite from Rupea some studies assign this type of zeolite an efficient ecological amendment.

Keywords: Adsorption, Desorption, Heavy metals, Soil, Wastewater.

Introduction

The water distribution in Romania is specified in the data published by the National Institute of Statistics and the National Administration Office of Water "Apele Române", in which according to, in 2019 the percentage of the general population who was connected to the public system of water distribution included 70.9% of the residents of our country, around 13 million recipients. In 2018, the statistics stated that the number of the public system water distribution recipients was with about 200.000 less than in

2019. The higher number registered in 2019 is due to the development of new supply networks (https://rowater.ro). The volume of the distributed water in 2019 was over one million m^3. Most of the distributed water was used for household aprovisionation (43.4%), followed by agriculture and pisciculture use (35,8%), various industries and construction (13.3%) and for other uses (7.5%) (https://rowater.ro).

However, a great interest is the great diversity of activities that produce wastewater, which are of an economic, household, urban, industrial, agricultural, meteorological, and social nature. Wastewater may contain varying amounts of pollutants or residues, which affect its physical, chemical, and bacteriological characteristics. At the European level, water is still limited due to the ever-increasing domestic and agro-industrial consumption, as well as climate change (Popa, 2011). In this context, we recall that one of the main objectives of the EU is to ensure the increased need for water resources for agricultural irrigation and other activities for urban development, the availability of water being essential for economic and social support (Popa, 2011).

Agriculture affects the availability of water for various economic and social sectors in both a quantitative and qualitative way, which justifies the treatment and use of technological wastewater, especially for irrigation. In many European countries, pollution caused by pesticides and fertilizers used in agriculture remains one of the main causes of water quality damage. It is also important to remember that with the ever-increasing need for water use among the population and both in the industrial and agricultural sectors alike are in constant competition with nature for the use of clean water.

The purpose of this paper is to update the data on the use of zeolites in technological wastewater treatment systems and devices, mainly aimed at the removal of heavy metals (Cd, Cr, Cu, Pb, Zn) from water and the increased bioavailability of these metals with severe consequences on soils, plants, and animals.

Data regarding the production and recovery of technological wastewater

The production, treatment, and disposal of wastewater in Romania. According to current data, in 2019 a total volume of approximately 1,896 million m^3 of wastewater was produced. Wastewater can contain various pollutants: organic, expressed by biochemical oxygen consumption of 5 hours (CBO 5), respectively chemical oxygen consumption (CCO-Cr), suspended particles, nutrients (nitrogen-NT, phosphorus-PT) or heavy metals (cadmium, copper, chromium, nickel, lead, zinc) (https://rowater.ro/). The same data shows that in 2019 the average daily concentrations of pollutants in wastewater generated in agriculture and fishing respectively in the food industry, reached considerable levels for CBO5 (2.3 and 23.2 respectively), CCO-Cr (3.3 respectively 61.7), suspended particles (0.7 and 21.4 respectively), NT (0.3 and 3.1, respectively) and PT (https://rowater.ro/).

The current national potential for wastewater treatment and discharge shows that in 2019, out of the total number of households residing in Romania, 54.3% were connected to the water distribution network, and the total volume of wastewater collected and discharged into natural receptors was approximately 1,870 million m^3, of which 631 million m^3 of wastewater was not subjected to any type of treatment.

Wastewater production, treatment and disposal in Europe and global level

In the EU, water is still a limited resource, as a third of the continent is facing stressful situations given the limited sources of water. The growing needs of the population and climate change are objective causes of water availability, so solving them will be a great challenge in the future. Excessive use of water resources, especially for agricultural irrigation, as well as for industrial and urban development works, is one of the main shortcomings in ensuring the EU's water needs. In this context, it is sufficient to mention the global impact of the 2003 drought, which mainly affected the Mediterranean countries, with economic losses estimated at at least EUR 8.7 billion (https://mmediu.ro; https://rowater.ro).

The immediate effects of the drought are also at the root of climate change. The frequency and intensity of droughts, as well as the subsequent damage, have risen sharply over the last 30 years, with the number of regions and people affected increasing by almost 20% (2022 Commission Work Program). The drought of the summer of 2017 illustrates even more convincingly the size of the economic losses, which in the Italian agricultural sector alone was 2 billion euros.

Wastewater treated by urban stations is a reliable alternative source of water supply for various purposes. Of these, agricultural irrigation offers the greatest opportunities for large-scale water reuse, thus helping to reduce Europe's water deficit (2022 Commission Work Program). Wastewater reuse has a lowerimpact on the environment than water transfers or desalination, and it also offers a wide range of environmental benefits. Although at present it is clear that the problems concerning the scarcity of water in the EU cannot be solved by reusing wastewater alone, as this practice is still far from reaching its full potential and differs greatly from one Member State to another.

The European Commission's work program (2017 and 2018) helps the EU's implementation of the Sustainable Development Goals on clean water and is expected to generate a significant increase worldwide of available clean water by 2030. The conditions of the recycling degrees and reuse of water are also contained within the work program. The European Parliament, through its resolution on the right to water of September 2015, supported by European citizens, (https://www.right2water.eu/) and the Committee of the Regions (through the amendment of December 2016 of the program "An efficient system of water management") encouraged the European Commission to develop a legislative framework on the reuse of wastewater.

The basics of the treatment and the rehabilitation of industrial wastewater

Under the pressure of declining global clean water sources, coupled with the growing population, it is becoming increasingly important to treat water and wastewater in the shortest time possible. Wastewater treatment consists of the removal of pollutants, by mechanical cleaning (removal of iron, magnesium), sterilization, desalination or softening, and the addition of specific supplements to improve the quality and some impact parameters, such as pH or electrical conductivity.

Water treatment includes various procedures available for the implementation of the necessary steps for this action, which by their nature can be (https://www.aerzen.com/en/contact.html; Rojanschi and Ognean, 1997):

- Physical for mechanical preparation, based on aeration, sedimentation or heat, performed in grills, filters, and sieves.
- Biological, including anaerobic treatment, biochemical oxidation or sludge digestion.
- Chemical, consisting of neutralization, disinfection, flocculation, and precipitation.
- Membranar, based on the use of filtration, osmosis and nano-filtration.

The procedures and phases of the treatment of the wastewater depend on the characteristics of the treatment plant, the treatment of wastewater, in general, involves the completion of specific steps.

Phase 1-mechanical treatment of wastewater

In this first stage, the wastewater is mechanically treated to remove the solid particles contained (about 20-30%), by being conducted in a grate installation, which filters the coarse impurities (leaves, paper, textiles) (https://www.aerzen.com/ro/contact.html). Various types of grills can be used, from coarse to fine, through which water passes at different speeds, making it easier to filter coarse materials step by step. The resulting waste is mechanically recovered, dried and moved to an incineration plant, and the water will pass into a sedimentation basin, with a relatively high flow rate (approximately 0.3 m/s), in order to further remove particles and coarse organic materials (stones, shards of glass, sand). The use of a round sand collector separates the substances from the wastewater by centrifugal force, which suctions in and then removes the impurities from the water. If no further recycling is possible, the waste from the sand collector shall be disposed of in a landfill or taken to an incineration plant.

Water purification in the mechanical treatment phase. In this important phase of mechanical water treatment, the speed flow rate of the water is reduced to approximately 1.5 cm/s. The lower speed rate of water and the bigger water basins facilitate the sedimentation of fine particles either on the surface of the water or on the bottom of the basins, depending on the nature of the impurities. The primary sludge isproduced by the sedimentation of organic materials. This type of sludge is collected from the bottom of the basin by a rake into a collection tank. The substances that float are transferred into a pipeline for floating sludge and then a pump transports the sludge into a tank for anaerobic digestion. In the anaerobic digestion tank methane gas is produced via four stages (hydrolysis, acidification, acetone generation, and the methanogens phase). The methane gas is then transformed into electricity in a heating block mill. The electricity can then be used to power the mill. The anaerobic digestion process is finished after approximately four weeks. The residues are represented by an odorless sludge resulting after centrifugal dehydration. This type of sludge is often used in agriculture. The mechanical treatment stage is thus at an end, and during this phase, approximately 30-40% of the impurities are removed. The water resulting from this phase can be used as such or it can undergo the next stage of the treatment process.

Phase 2-biological purification of wastewater

Most water treatment plants are equipped with aeration tanks, which are also known as circulation tanks. The prepurified water is transported into these tanks which are destined for biological purification. In the aeration tanks the biological processes are facilitated by the movement of the water (https://www.aerzen.com/ro/contact.html). Thus, through oxygen supplementation and with the help of propellers ventilated areas are created, in which various environmental conditions are created for bacteria and other microorganisms. These microorganisms feed off contaminating substances that are present in the water and later transform them into inorganic substances. The bacteria create activated sludge clumps that float freely in the water and their multiplication accelerates the forming of activated sludge. Wastewater with activated sludge is then transported into the secondary epuration tank where the flow velocity is reduced once again. The activated sludge is deposited at the bottom of the tank where it can be separated by mechanical cleaning devices located in the inferior part of the basins. A part of the sludge is transferred into the fermentation tower as supplementary biomass and the remaining sludge, which at this stage is also called return activated sludge, is restored into the aeration tank to ensure a sufficient number of microorganisms in the aeration tank so that the decomposition process can continue properly. After the biological treatment, approximately 90% of the wastewater is cleared of biodegradable substances. Because of the compressor oxygen supplementation, the biological stage is the most energy-consuming and expensive phase. In most cases biological purification is not enough, thus the third step which is the chemical phase is required.

Phase 3-chemical wastewater treatment

This phase is based on chemical processes that restore the water to standard physicochemical parameters through neutralization, sanitization, the precipitation of phosphates, and the elimination of nitrogen and manganese (https://www.aerzen.com/ro/contact.html). The neutralization process improves the pH level of the water, and the chlorine or carbon dioxide sanitization eliminates pathogens. A good alternative to chemical treatment is ultraviolet radiation which is rarely used. The elimination of phosphates, derived from detergents, fertilizers, food additives, and feces, is also essential because they can facilitate the multiplication of microorganisms if they remain in the wastewater. Phosphate precipitation is partially triggered by the addition of aluminum or iron salts to the collector sand or to the secondary treatment tank. The metal phosphate flakes, which form during this secondary purification, are then collected with the activated sludge. The chemical purification of wastewater also includes the removal of nitrogen, as nitrogen compounds are oxygen consumers, thus being harmful for fish. Nitrogen is removed by nitrification and denitrification and is converted to nitrite, and after that into nitrate by adding anaerobic bacteria and oxygen. Subsequent denitrification is triggered by the addition of anaerobic microorganisms, which by enzymatic activities break down nitrate into nitrogen gas, which is then released into the atmosphere. Iron cations are oxidized by the addition of oxygen and caustic soda to wastewater. The removal of manganese, usually present in wastewater as manganese bicarbonate, is due to the addition of oxygen which forms manganese compounds 4, which are difficult to dissolve and easily removed from the water.

Phase 4-wastewater nanofiltration

In the fourth and final stage of purification, membrane processes and filters are used. This stage is combined with chemical precipitation and flocculation processes, such as the flocculation filtration method. Precipitators and flocculants are added to the wastewater, which causes the flocculation of different types of substances. The wastewater with the flocculated material passes through a cloth or sand filter. Nanofiltration works in a very similar way, with water being passed under pressure through a membrane that retains even the smallest dissolved particles, such as molecules or ions of heavy metals. The same thing happens with reverse osmosis. Pollutants retained during filtration, nanofiltration, and reverse osmosis, generate the filter sludge. The water finally reaches the last area of the wastewater treatment plant, represented by the treated water storage basin. Water samples are taken again for quality check, and the purified water will be returned to the hydrological circuit if it meets the legal standards.

The physico-chemical analysis of zeolites used in wastewater and soil treatments

Bioavailability is a characteristic of pollutants in general, which consists in their ability to penetrate and distribute in the tissues of living organisms (Egene et al., 2018). It has been found that some soil amendments can reduce the bioavailability of heavy metals by activating adsorption, complexation and precipitation processes, as well as reactive minerals such as zeolites, phosphate rocks, carbonates and clay minerals (Vrinceanu et al., 2019; Senila et al., 2022). These ecological amendments are effective and do not affect the quality of treated soil and water (Zheng et al., 2021). The physical and chemical properties of zeolites are given by their morphology, particle size, thermal expansion, density, hardness, compositional uniformity, optical properties, color, electrical conductivity, thermochemistry, and structure of internal tetrahedra and external bonds (Filippidis et al., 1996). Various chemical elements have been identified in the composition of zeolites: Fe, Ca, Mg, Na, P, Cu, Zn, Mn, Si, Al, Cr, and S. Ion exchange is an important property of zeolites, which consists of physical-chemical properties that are dependent on pH, temperature, and the characteristics of cations that are subjected to substitution (Filippidis et al., 1996; Leyva et al., 2004; Senila et al., 2022). The negative charge of zeolites is neutralized by the positive charge of the cations inside the pores. The negative charge of the zeolite molecule is counterbalanced by cations that can participate in ion exchange (Coombs et al., 1997; Correia, 2003).

The adsorption of large organic molecules (herbicides, fungicides, pesticides, mycotoxins, drugs, and biologically active molecules) is ensured by the pore volume and the zeolitic structure (Breck, 1974; Colella, 2007). The results of the study carried out by Ulmanu et al., (2006) regarding the evaluation of the capacity of a natural zeolite from Baia Mare (Table 1) to adsorb some heavy metals (lead, copper, zinc, cadmium and manganese) from soils and corn, mustard and oat crops. Senila et al., (2022) conducted research on a zeolitic granular material (0-0.5 mm) of Rupea (Table 1) which was mechanically activated and heat-treated at different temperatures and loaded with nutrients. The investigations were carried out by the processing and measuring equipment (sieving system, thermobalance, SEM and XRF to determine the chemical composition and granulation) of Zeolites Production Rupea laboratories. The equipment of ICIA Cluj-Napoca was also used to determine the release of nutrients and pesticides from the structure of zeolites (SpectraMax iD3 spectrometer, Molecular; gas-chromatograph with electron capture detector, type GC Agilent 7890A). The study protocol consisted in determining the chemical composition and grain size of the zeolitic material and also testing the desorption of the soil treated with activated zeolite (for 5 days). The soil was analyzed before and after the application of the zeolitic material and the content of ammonium, inorganic phosphorus and some pesticides was measured. Regarding the immobilization of heavy metals, two experiments were initiated in pots with zeolite-treated soil, in which the evolution of pH and metal concentrations of the soil (Csol) were investigated. The heavy metal levels were evaluated using the diffusible gradient technique (CDGT).

Among the results obtained by Senila et al., (2022) research are the following: the pH level of the soil was maintained at the initial values; a decrease of the average concentration of heavy metals in the soil was registered after 3 months of storage, apart from zinc; the Csol and CDGT exams recorded a similar trend in the evolution of heavy metal concentrations; the addition of zeolites in the soil caused a significant reduction in Cd and Pb concentrations and also a decrease in the bioavailability of copper, chromium and zinc. Based on the data obtained after the analysis of the heavy metal contaminated soil samples (Senila et al., 2022) treated with zeolite, the authors concluded that natural zeolites are an ecologically effective amendment for immobilizing heavy metals from soil and wastewater. Among the quantitative determinations that were performed, the following formula for the calculation of the nutrient desorption efficiency in an artificial environment was elaborated:

Desorbant effiiency (Ed; %)=Initial concentration (Co)-The concentration after desorbtion (Ce) x 100

Table 2 shows the values obtained during the desorption tests for some components of the soil treated with zeolitic material: ammonia, phosphorus, fenvalerate, cypermethrin and fenhexamide. The granulation size of Rupea clinoptilolite samples varied between 0 and 0.5 mm. The analysis of the chemical composition of Rupea zeolites stated the following: a variation between 56.85% and 59.31% of the SiO_2 content; a variation between 11.94% and 12.88% of the Al_2O_3 content: a ratio 4 times higher of Si/Al, compared to the one generally found in the structure of zeolites, which is specific to clinoptilolite. Other major compositional constituents of the clinoptilolite samples had the following concentrations: CaO 2.67%-2.83%; K_2O 2.30%-2.40%; Fe_2O_3 1.24%-1.59% of Fe_2O_3 and MgO 1.42%-1.62%. The overall analysis of the data confirmed a reduced variability of the chemical composition of Rupea clinoptilolite.

The action of zeolitic devices used in the treatment of technological wastewater. In 2016, Koshy et al. conducted a study in which they used zeolites to decontaminate wastewater and as reactive permeable barriers. Due to their extremely high porosity, zeolites can retain water and even alcohol up to 60% of their weight (Burmanczuk et al., 2016; Zhang et al., 2013). Water molecules in zeolitic pores can easily evaporate or reabsorb without structurally damaging the zeolitic material, which is a permanent reservoir of water and can maintain moisture during dry periods.

The efficiency of zeolites in the adsorption process of petroleum products from gaseous and aqueous media has also been intensively studied, and the results obtained made it possible to recommend this material as an adsorbent for various hydrocarbons (Mishra and Jain, 2011; Micle et al., 2010; Popa et al., 2018). Of great interest are the results that have proven the special adsorbent effect of clinoptilolite for lead, aluminum, zinc, iron, cesium and especially cobalt from wastewater (Neag et al., 2020; Varvara et al, 2018; Wen et al., 2018).

The disposal of nuclear waste and hazardous materials is an important use of zeolites (Cătuneanu et al., 2010; Luz et al., 2012; Simical et al., 2015; Vignola et al., 2011). All research conducted on environmental protection is concerned with the effects of zeolites on the treatment of contaminated groundwater or other categories of technological wastewater, including those used in some livestock farms and food processing units. Zeolite filters (with ZSM-5 and Mordenit) are currently used as long-term decontaminants of hydrocarbon and dissolved inorganic salts polluted groundwater (Vignola et al., 2011).

Table 1. Physical, chemical and mineral characteristics of Rupea zeolites and Baia-Mare zeolites (Zeolites Group; Ulmanu et al., 2006).

Characteristics of Rupea zeolites

Physical characteristics		**Chemical comp. (%)**		**Mineral comp. (%)**	
Softening point (°C)	1250	SiO_2	68.75-71.3	Clinoptilolit	87-90
Melting temperature(°C)	1320	Fe_2O_3	1.90-2.1	Plagioclaz	2-5
Melting flow temperature (°C)	1400	Al_2O_3	11.35-13.1	Anherit	2-3
Color	Gri-verde	MgO	1.18-1.20	Cristobalit	4-5
Smell	Inodor	CaO	2.86-5.2	Clinoptilolit	87-90
Porosity (%)	32-44	Na_2O	0.82-1.30	Plagioclaz	2-5
Pore diameter (nm)	0.4-0.6	K_2O	3.17-3.40	Anherit	2-3
Durity-Mohs scale	3.5-4	P.C	8.75-8.86	Cristobalit	4-5
Water absorbtion (%)	34-36	SiO_2	68.75-71.3		
pH	8.75	Fe_2O_3	1.90-2.1		
Density	2.377				

Characteristics of Baia-Mare zeolites

Parametre	**Value**
Main component-clinoptilolite	Up to 80%
Quartz	4-5%
Feldspat	3-4%
Mordenite	1-2%
SiO_2/Al_2O_3 ratio	5.6
Surface (B.E.T, m^2/g)	52.0165 ± 0.2833
External surface(m^2/g)	45.7051
Micropore surface (m^2/g)	6.3115
Micropore volume (cm^3/g)	0.002466
Pore diameter (mean value), Å	101.8246
CEC (meq/g)	1.5105
SiO^2 (%)	64.58
Al^2O^3 (%)	11.49
CaO (%)	1.19

MgO (%)	0.33
Na_2O (%)	2.50
K_2O (%)	2.55
Fe_2O_3 (%)	1.31
H_2O (%)	12.92
Other (%)	3.13

Table 2. Physico-chemical properties of natural zeolite (NZ), control soil (CS) and mixtures with zeolites (NZS_3 and NZS_6) at the start of experiments (average ± standard deviation, n=3 parallel determinations) (Senila et All., 2022).

Parametre	**NZ**	**CS**	**NZS_3**	**NZS_6**
pH	9.55 ± 0.20	8.58 ± 0.12	8.77 ± 0.15	8.78 ± 0.15
Cd (mg kg^{-1})	<1.0	34.7 ± 1.7	33.6 ± 1.8	31.4 ± 1.2
Cr (mg kg^{-1})	<1.0 34.7 ± 1.7	33.6 ± 1.8	14.7 ± 0.5	14.7 ± 0.6
Cu (mg kg^{-1})	1.16 ± 0.12	553 ± 24	522 ± 20	516 ± 15
Pb (mg kg^{-1})	6.33 ± 0.43	392 ± 25	378 ± 18	366 ± 19
Zn (mg kg^{-1})	4.40 ± 0.38	2779 ± 110	2800 ± 87	2742 ± 65
CEC (meq/100 g)	129 ± 6.5	60.2 ± 4.1	62.4 ± 3.5	61.5 ± 3.1
Cr (%)	<0.01	2.65 ± 0.14	2.58 ± 0.21	2.52 ± 0.17
Nr (%)	<0.01	1.10 ± 0.06	1.04 ± 0.06	1.05 ± 0.10
SiO_2 (%)	71.79 ± 1.12			
Al_2O_3	11.19 ± 0.35			
CaO (%)	2.64 ± 0.04			
MgO (%)	0.66 ± 0.02			
K_2O (%)	2.50 ± 0.10			
Na_2O (%)	0.52 ± 0.02			
Fe_2O_3	1.55 ± 0.03			
MnO (%)	0.03 ± 0.003			
Others (%)				

*Threshold for sensitive use according to Romanian legislation (23). **Maximum levels in the sewage sludges intended for the application on agricultural soil (zeolite was associated in this study with a soil amendment) (24).

Conclusion

Zeolites can retain and remove heavy metals and ionic species from polluted soils and wastewater therefore they can be used in environmental protection and ecology. Zeolites are also excellent sorbents medium for permeable reactive barriers. The data included in this review is a set of relevant documentation for the analysis of wastewater treatment and recycling procedures, as well as heavy metal contaminated soils, with special reference to the use as the adsorbent substrate of Rupea and Baia Mare zeolites. Insignificant variations of the main zeolitic components were found: SiO_2 (56.85-59.31%), Al_2O_3 (11.94-12.88%), CaO (2.67-2.83%), K_2O (2.30-2.40%), Fe_2O_3 (1.24-1.59%), MgO (1.42-1.62%). The Si/Al ratio was found to be 4 times higher, which is specific to clinoptilolite (Popsa et al., 2018). The treatment with Rupea clinoptilolite of heavy metal contaminated soil samples (Cd, Cr, Cu, Pb, Zn) proved to be an effective ecological amendment for the immobilization of nutrients and heavy metals, according to the following formula: Desorption efficiency=Initial concentration-Desorption concentration x 100.

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