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INVESTIGATIONS ON THE EFFECTIVENESS OF WASTEWATER PURIFICATION IN MEDIUM SAND WITH ASSISTING CLINOPTILOLITE LAYER

Model investigations of wastewater purification were carried out in a medium sand bed with an assisting natural clinoptilolite layer 0.10 or 0.25 m thick. The effectiveness of wastewater purification related to basic qualitative parameters was in accordance with the Polish standards on sewage disposal into grounds and surface water. Medium sand soil bed with the assisting natural clinoptilolite layer 0.25 m thick showed on average the removal efficiency regarding TSS higher by 3.3%, total nitrogen by 29.3%, total phosphorus by 25.9%, reduction efficiency regarding BOD_5 by 1.1% and COD by 15.9% than that with the thinner clinoptilolite layer. The investigations confirmed that natural clinoptilolite with the granulation 1–5 mm can be used to enhance the removal of nitrogen and phosphorus compounds from wastewater with the application of infiltration drainage. However, very good effect of the TSS removal from the wastewater in the investigated soil beds can lead to their fast clogging under the infiltration drainage. Septic tanks should be designed in such a way that they retain as much TSS as possible, e.g., multi-chamber tanks instead of one-chamber ones.

1. INTRODUCTION

Household wastewater treatment plants are used in scattered housing areas where it is economically ungrounded to build sewerage systems. Domestic wastewater can be disposed into the ground if it comes from free-standing houses localized behind the underground water protection zones, if the sewage amount does not exceed 5.0 m^3 per day as well as if its BOD_5 is reduced by at least 20% and TSS amount – by at least 50%. Household wastewater treatments with infiltration drainage are built in well permeable soils when the highest usable groundwater level of underground water is placed at least 1.5 m under the sewage infiltration level.

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Infiltration drainage is a device serving to introduce domestic wastewater into the ground after its provisional purification in a septic tank. As a result of percolation through natural soil layers, the wastewater is subjected to processes of biological purification under the influence of aerobic bacteria and other microorganisms which take up oxygen from the ground air. Fine solid particles and colloids are retained on the surface of ground grains. Part of the wastewater being filtrated in the ground is taken up by plant roots, other part raises towards the ground surface in ground capillaries, from where water evaporates, the remaining amount percolates into underground water.

Too high loading of a soil bed by sediments and colloid particles results in a decrease of a ground permeability [1] and in so-called filtration (clogging) cake which forms on a ground surface and pores [2, 3]. The TSS amount in raw wastewater flowing out from a septic tank into the soil bed can fluctuate between 20 $g \cdot m^{-3}$ and 475 $g \cdot m^{-3}$ [2]. Microscopic analyses showed that the filtration (clogging) cake, forming in the soil, contains mainly filamentous fibers of toilet paper which is washing out from the septic tank and does not undergo biodegradation [2].

The investigations carried out for a medium sand soil bed show that the average removal efficiency regarding total nitrogen (22%) and total phosphorus (23%) is small. Moreover, other scientists confirmed [4, 5] that the efficiency of removal of total nitrogen and total phosphorus from the sewage purified by well-permeable ground is small. Large number of household wastewater treatment plants with infiltration drainage on a given area can lead to pollution of underground water with compounds of nitrogen [6] and phosphorus [7]. However, the nitrogen and phosphorus compounds accumulated in the soil bed under the infiltration drainage can be successfully used by plants [8]. Currently, minerals and soils are being sought [9] which could be used as layers improving the effectiveness of wastewater purification in soil beds under the infiltration drainage of wastewater.

The objective of these investigations is to check under laboratory conditions whether a natural clinoptilolite assisting layer with the granulation of 1–5 mm introduced into the ground may improve the efficiency of removal of nitrogen and phosphorus compounds from wastewater. For this purpose, model medium sand soil beds with clinoptilolite layers 0.10 m and 0.25 m thick were applied, placed under the infiltration drainage of wastewater.

2. CHARACTERISTICS OF CLINOPTILOLITE

Clinoptilolite (($K,Na,1/2Ca)_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 8H_2O$) is the most popular zeolite in the nature. It belongs to the series of heulandites, minerals characterized by significant variability of Si/Al ratio. It is a natural aluminum silicate with skeleton structure containing free spaces filled with big ions (Ca^{2+}, Mg^{2+}, Na^+, K^+) and water molecules. The silica content ranges from 54.4 to 66.6 wt. %, and that of aluminum oxide from 13.8 to

18.53 wt. %. The specific density of the clinoptilolite ranges from 2.02 to 2.25 g/cm^3 and its Mohs scale hardness – from 3.5 to 5.5 [10]. The composition of its elementary cell is $(K_2Na_2Ca)_2 \cdot [(Al_6Si_{30})O_{72}] \cdot 24H_2O$. Clinoptilolite is a porous material, characterized by good sorption, ion changeability and catalytic properties which can be modified chemically. It has a high thermal resistance and significant chemical resistance against acids [10].

Large deposits of clinoptilolite have been proven in USA, Mexico, the Eastern and Southern Europe, China and Japan. Clinoptilolite is found in plutonic rocks in Slovakia, Ukraine and Hungary. In Poland, it occurs mainly in sedimentary rocks near Rzeszów and Cracow as well as in Lower Silesia. [10].

Clinoptilolite is applied on an industrial scale as a filtration bed for removing compounds of iron and manganese as well as sediments, colloid particles, phytoplankton and bacteria from water [10, 11]. It is used to absorb odors in poultry and pig farms, i.e., to remove nitrogen oxides [12]. Investigations are also carried out on the application of the clinoptilolite in veterinary medicine [13] and as a remover of trace metal ions [14], nitrogen compounds [15], phosphates [16] and radioactive elements [17] from water; trials have been undertaken on application of the clinoptilolite to purify municipal and refinery wastewater.

3. METHODOLOGY OF INVESTIGATIONS

A measuring stand was built in the form of a hermetic tank 1.20 m long, 0.20 m wide and 1.70 m high (Fig. 1). The tank was made of plastic plates (9) mounted in metal frames (11). Wastewater from the tank (1) was transported with a pump (2) started by a controller (3) through a delivery pipe (4) to a drain line (5) 100 mm of the diameter, placed in a bed layer (6) made of stones of the diameter of 20–40 mm. The dimensions of the drainage bed layer were: length 0.50 m, width 0.20 m, height 0.20 m. The wastewater flowed to the drainage bed layer through an outlet of 8 mm in diameter in the bottom of the drainage pipe. Then, after passing the drainage layer, it flowed through an assisting layer (7) into a soil bed (8).

The investigations were carried out using the medium sand soil bed with the assisting natural clinoptilolite layer of the thickness of 0.1 or 0.25 m and granulation 1–5 mm. The thickness of the sand soil bed was 1.30 m. Three openings (10) were made in the bottom of the measuring stand to enable outflow of the sewage drained through the assisting layer and soil bed to the collecting vessels (12). The soil was layered in the tank, wherein each layer had the thickness 0.10 m and then all layers were compacted (the degree of compaction was not determined). The ventilation of the drainage bed (6) occurred through the drain line (5).

The soil in the tank was compacted layer-by-layer with use of low pressing force – not the whole soil in the tank was compacted at once because there was a risk that in

such a case the tank might have become unsealed. Moreover, as is well known, the best effects of soil compaction are obtained if soils are compacted layer-by-layer.
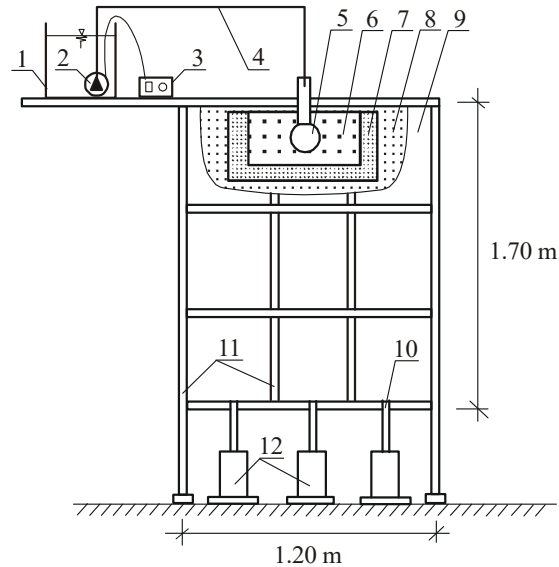

Fig. 1. Schematic diagram of the measuring stand: 1 – tank, 2 – pump, 3 – controller,
4 – delivery pipe, 5 – drain line, 6 – drainage bed, 7 – natural clinoptilolite assisting layer,
8 – medium sand soil bed, 9 – transparent plastic plate, 10 – wastewater outflow,
11 – metal frame, 12 – effluent collecting vessels

The model wastewater was used in the investigation, made according to the standard PN-C-04616/10 of distilled water and the following compounds: enriched dry broth, peptone, urea, anhydrous sodium acetate, soluble starch, grey soap, crystalline calcium chloride, magnesium sulfate, sodium chloride, potassium chloride. The sewage was dosed twice a day and its daily quantity was determined in dependence on the type of the soil bed and its minimum hydraulic loadability with wastewater according to the Polish recommendations. The wastewater, both before its introduction in the bed, and after its drainage through the soil bed with the assisting layer, was physically and chemically analyzed in order to determine the values of the following indicators: TSS, BOD_5, COD, total nitrogen, total phosphorus, ammonium nitrogen, nitrate nitrogen, nitrite nitrogen, pH. The individual indicators were determined once a week with consideration of the wastewater filtration time of the soil bed with the 0.10 or 0.20 m thick assisting layer. Contents of the grain size distribution of the soil granulation were determined by the sieve analysis. Three samples of the medium sand were subjected to the granulometric tests and the obtained results are presented in Fig. 2. Based on the tracer tests, it was determined the drainage time of the wastewater through the sand soil bed, equal to 18 h.
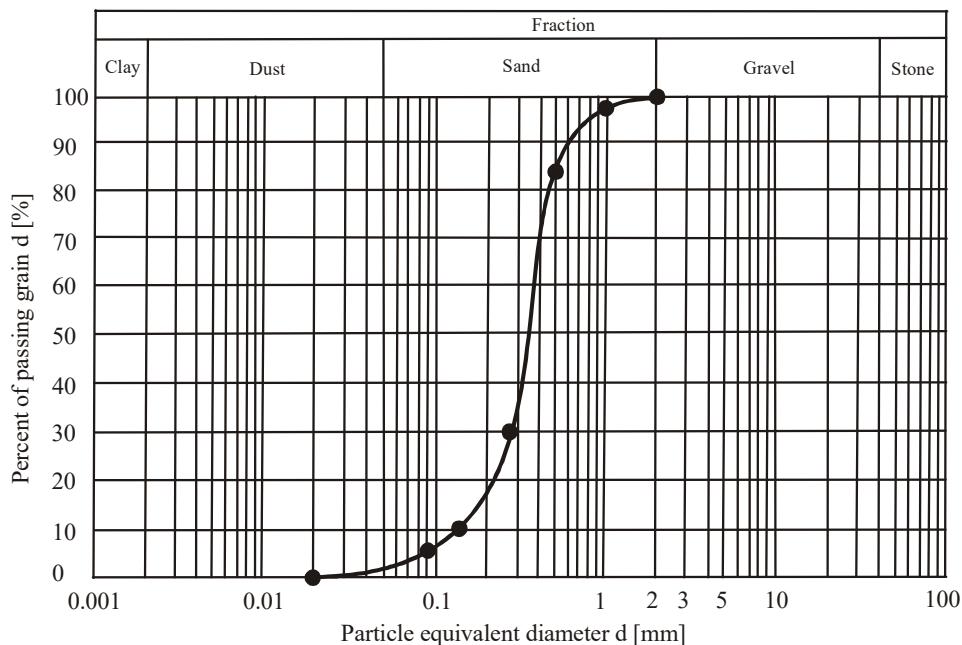
Fig. 2. Grain size distribution – medium sand

According to the Polish recommendations, a daily sewage dose must be related to the length of the drainage line. The hydraulic load of the drainage line is related to the 1 m long line and for the medium sand it is equal to 15 $dm^3 \cdot m^{-1} \cdot day^{-1}$. Therefore, the daily wastewater dose should be 3 $dm^3 \cdot day^{-1}$. This dose was divided into three equal portions, dosed on the drainage bed at 7 a.m., 3 p.m. and 11 p.m.

The model wastewater was prepared every six days and the wastewater quality indicators were determined always on the beginning, in the middle and on the end of its dosing time. The temperature in the room was equal to 14 °C throughout the entire test period. The TSS content was determined by weighing, BOD_5 – by the electrochemical method, COD – by titration with potassium dichromate; total nitrogen, total phosphorus, ammonium nitrogen, nitrate nitrogen, nitrite nitrogen – using colorimetric methods, pH – by the electrometric method.

4. DISCUSSION OF THE RESULTS

The formation of biologically active layer in the medium sand soil bed with the natural clinoptilolite layer lasted 11 weeks. During the wastewater filtration through the investigated soil bed, under the drainage layer, a grey, 2.0–2.5 cm thick biological film

formed which was a habitat for bacteria and other microorganisms. During the investigations, the soil bed (medium sand) was saturated with wastewater (it was wet) but the sewage did not stagnate in the soil bed during filtration. The ventilation of the drainage bed took place through the drain line.

Table 1 contains average values of the contamination indicators of raw wastewater and the wastewater purified on the medium sand soil bed with the assisting natural clinoptilolite layer, in dependence on the layer thickness (0.10 or 0.25 m) and on the measuring stand operation time (12–15 weeks). After the drainage of the model sewage through the sand soil bed with the assisting clinoptilolite layer, the following indicators reduced their values: BOD_5, COD, TSS, total nitrogen, ammonium nitrogen and total phosphorus. The nitrite nitrogen occurred in the purified sewage at trace level, whereas the nitrates content and pH increased.

Table 1

Characteristics of wastewater quality before and after purification
in medium sand with assisting clinoptilolite layer (average values)

Indicator, unit	Raw wastewater				Purified wastewater				Standard
	Operation time [week]								
	12	13	14	15	12	13	14	15	
Thickness of assisting clinoptilolite layer 0.10 m									
TSS, $g \cdot m^{-3}$	148.4	144.9	135.6	133.8	40.1	38.8	38.3	37.4	50
BOD_5, $g\ O_2 \cdot m^{-3}$	141.2	129.3	122.7	114.5	2.6	2.2	1.9	1.6	40
COD, $g\ O_2 \cdot m^{-3}$	252.5	258.7	249.4	247.8	24.9	18.5	22.4	17.8	150
Total nitrogen, $g\ N \cdot m^{-3}$	37.1	36.8	35.4	36.7	26.9	27.4	27.1	26.7	30
Ammonium nitrogen, $g\ N\text{-}NH_4^+ \cdot m^{-3}$	0.96	0.90	0.96	0.93	0.11	0.12	0.10	0.09	–
Nitrate nitrogen, $g\ N\text{-}NO_3^- \cdot m^{-3}$	0.88	0.89	0.85	0.83	12.82	13.14	12.67	12.75	–
Nitrite nitrogen, $g\ N\text{-}NO_2 \cdot m^{-3}$	0.025	0.024	0.026	0.021	0.012	0.008	0.006	0.006	–
Total phosphorus, $g\ P \cdot m^{-3}$	1.74	1.72	1.79	1.71	0.93	0.76	0.70	0.64	5
Reaction, pH	7.23	7.28	7.24	7.20	7.41	7.44	7.48	7.37	–
Thickness of assisting clinoptilolite layer 0.25 m									
TSS, $g \cdot m^{-3}\ N\text{-}NO_2^-$	134.6	134.9	132.8	134.1	33.1	32.6	32.5	31.7	50
BOD_5, $g\ O_2 \cdot m^{-3}$	116.7	114.8	114.3	114.4	1.1	1.1	0.7	0.7	40
COD, $g\ O_2 \cdot m^{-3}$	246.8	240.9	261.6	258.4	13.6	12.7	11.7	11.5	150
Total nitrogen, $g\ N \cdot m^{-3}$	35.2	36.1	35.8	35.5	17.9	16.5	14.9	14.3	30
Ammonium nitrogen, $g\ N\text{-}NH_4^+ \cdot m^{-3}$	0.91	0.97	0.95	0.94	0.08	0.05	0.03	0.02	–
Nitrate nitrogen, $g\ N\text{-}NO_3^- \cdot m^{-3}$	0.96	0.92	0.95	0.96	10.84	10.86	10.75	10.56	–
Nitrite nitrogen, $g\ N\text{-}NO_2 \cdot m^{-3}$	0.018	0.019	0.017	0.017	0.004	0.002	0.003	0.004	–
Total phosphorus, $g\ P \cdot m^{-3}$	1.62	1.67	1.64	1.71	0.39	0.31	0.24	0.23	5
pH	7.56	7.43	7.41	7.52	7.68	7.59	7.64	7.71	–

The average TSS removal efficiency in the soil bed with the clinoptilolite layer 0.10 m thick amounted to 72.5% and with the 0.25 m clinoptilolite layer – 75.8%. Attention should

be paid to high TSS retention efficiency of the investigated soil beds. TSS being introduced to a soil bed in a large quantity causes its fast clogging and formation of a biological film under the infiltration drainage [18] which reduces the permeability of the soil bed [19] and limits the life of an infiltration drainage purification plant. A characteristic sign of such clogging are odors coming out through drainage vent chimneys – the wastewater is retained in the drainage bed and oxygen cannot reach it, inducing oxygen-free conditions and rendering the bed unfit to fulfil its function. In such a situation, it is inevitable to dig out the drainage and lay it in a new place where the soil is not clogged. The drainage lines must be laid no closer than 1.5 m from the previous localization. Examinations carried out [20] show that the soil bed under the infiltration drainage is a popular habitat of earthworms which loosen the bed (make vertical and horizontal channels) and thus increase the bed permeability. According to Spychała and Pilc [21], if earthworms are introduced into a clogged soil bed under infiltration drainage, within two weeks they increase its permeability (de-clog it) and decrease the quantity of organic substances in the bed. The average efficiency of the BOD_5 and COD reduction in the soil bed with the clinoptilolite layer 0.1 m thick amounted 98.1 and 79.2%, respectively, whereas in the soil bed with the layer 0.25 m thick – 99.2 and 95.1%, respectively.

The investigations carried out showed that the well-permeable soil with the assisting layer had high efficiency of removal of impurities from the wastewater. The results of laboratory tests carried out by other researchers [5, 22] also confirm the high efficiency of BOD_5 and COD reduction in the sewage after its purification in a well-permeable soil.

The average total nitrogen removal efficiency in the soil bed with the layer of clinoptilolite 0.10 m thick amounted to 26.0% and with the layer 0.25 m thick – 55.3%. The application of the assisting layer consisting of natural clinoptilolite improved the average total nitrogen removal efficiency related to the bed consisting only of sand where the average total nitrogen removal efficiency amounted to 22%. The ammonium nitrogen removal efficiency in the soil bed with the 0.10 m thick clinoptilolite layer was high and amounted to 88.8% in average, wherein the nitrate nitrogen content in the purified wastewater increased 15 times in average. In the soil bed with the 0.25 m thick clinoptilolite layer, however, the ammonium nitrogen removal efficiency was even higher and equal to 95.2% in average, wherein the nitrate nitrogen content in the purified sewage increased only 11 times in average. Low ammonium nitrogen content and high nitrate nitrogen content in the purified sewage in the investigated soil bed proves very good conditions of the nitrification process what implies that nitrifying bacteria are well immobilized on the natural clinoptilolite. This phenomenon is described in the literature [15, 16]. The pH reaction increased by 2.5% on average in the purified wastewater (for both investigated soil beds).

The phosphorus is removed from soil bed mainly in adsorption and precipitation processes as well as it is absorbed by plants. The efficiency of the adsorption and precipitation processes depends on the pH value, redox potential, presence of ions of iron,

aluminum and calcium in soil bed, on the native phosphorus content in the bed as well as on its sorption capacity. In the soil beds having light acid or neutral reaction, the dominant role in the adsorption process is attributed to the iron and aluminum compounds which adsorb the phosphorus in form of insoluble complex compounds causing its long-lasting retention. In the alkaline soil beds, however, the phosphorus adsorption processes occur thanks to the calcium compounds, with which the phosphorus creates permanent mineral combinations. Examinations showed that the total phosphorus removal efficiency for the soil bed with the 0.10 m thick assisting clinoptilolite layer amounted to 56.5% and for the soil bed with the layer 0.25 m thick – 82.4%. The application of the natural clinoptilolite assisting layer in the medium sand soil bed significantly improved the total phosphorus removal efficiency related to the bed consisting only of sand where the total phosphorus removal efficiency amounted to 23% in average. The results showed (Table 1) that the natural clinoptilolite with granulation 1–5 mm, characterized by high porosity, is an efficient adsorbent of phosphorus compounds.

Table 2

Results of calculations of the *t*-Student statistics

Parameter, thickness of assisting layer	Average	Standard deviation	Difference between average values	Standard deviation for values	$|t_{cal}|$	p_{cal}
TSS, 0.10 m	38.650	1.127	6.175	0.591	20.900	0.000240
TSS, 0.25 m	32.475	0.580				
BOD$_5$, 0.10 m	2.075	0.427	1.175	0.250	9.400	0.002551
BOD$_5$, 0.25 m	0.900	0.231				
COD, 0.10 m	20.900	3.348	8.525	2.876	5.929	0.009588
COD, 0.25 m	12.375	0.971				
Total nitrogen, 0.10 m	27.025	0.299	11.125	1.565	14.217	0.000754
Total nitrogen, 0.25 m	15.900	1.625				
Ammonium nitrogen, 0.10 m	0.105	0.013	0.060	0.020	6.000	0.009273
Ammonium nitrogen, 0.25 m	0.045	0.026				
Nitrate nitrogen, 0.10 m	12.845	0.206	2.093	0.170	24.565	0.000148
Nitrate nitrogen, 0.25 m	10.753	0.137				
Nitrite nitrogen, 0.10 m	0.008	0.003	0.005	0.003	3.450	0.040943
Nitrite nitrogen, 0.25 m	0.003	0.001				
Total phosphorus, 0.10 m	0.758	0.125	0.465	0.054	17.075	0.000438
Total phosphorus, 0.25 m	0.293	0.074				
pH, 0.10 m	7.425	0.047	–0.230	0.091	–5.039	0.015067
pH, 0.25 m	7.655	0.052				

$|t_{cal}|$ – obtained *t*-Student statistics value, p_{cal} – obtained probability value, t_α read from the tables for $p = 0.05$ and $v = 6$ is 2.447. The differences of average values are significant with probability $p < 0.05$.

Statistical analysis was also carried out in order to check whether the differences in average values in the results of removal of impurities (Table 1) are statistically significant. A *t*-Student test was applied for two populations: according to the zero hypothesis (H_0: $m_1 = m_2$) the differences between the average values are statistically equal to each other and according to the alternative hypothesis (H_1: $m_1 \neq m_2$) these differences are statistically different. Calculations of the value of *t*-Student statistics $|t_{cal}|$ were performed with the use of the STATISTICA program and the obtained results are shown in Table 2.

For the alternative hypothesis, a critical area $|t_{cal}| \geq t_{\alpha = 0.05}$ was determined and for $v = m_1 + m_2 - 2 = 6$ degrees of freedom and $\alpha = 0.05$ (the assumed 5% risk of error, i.e., significance level) a critical value $t_{\alpha = 0.05} = 2.447$ was obtained from the tables of the *t*-Student distribution. Table 2 shows that $|t_{cal}| \geq t_{\alpha = 0.05}$, thus the zero hypothesis must be rejected and it can be concluded that the differences of average values in the results of removal of impurities from sewage for 0.10 and 0.25 m thick natural clinoptilolite assisting layers are statistically significant. It was also confirmed by the calculated probability value − p_{cal} being lower than 0.05 (assumed significance level).

5. CONCLUSIONS

Wastewater purified in the model sand soil beds with natural clinoptilolite of the granulation of 1–5 mm fulfilled the Polish recommendations for its disposal into ground regarding basic quality indicators (TSS, BOD₅, COD). The medium sand soil bed with the assisting natural clinoptilolite layer 0.25 m thick was more effective than the bed 0.10 m thick.

Natural clinoptilolite of the granulation of 1–5 mm can be used to improve removal of nitrogen and phosphorus compounds from wastewater with the application of infiltration drainage. To address problems with clogging, septic tanks should be designed in such a way that they retain as much as possible of TSS, e.g., in multi-chamber tanks.

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