The dairy industry is generally considered a major consumer of water and the largest source of wastewater per unit product (0.2 to 10 L of wastewater per liter of processed milk [1]) in the food industry. All production phases in the dairy industry, such as packaging, transport, storage and distribution, have a significant impact on the environment [2]. The dairy industry wastewater is characterized by high concentrations of organic matter (proteins, carbohydrates and fats), suspended solids, nitrogen, high biological (BOD) and chemical oxygen demand (COD) [1-2]. Some particular dairy industry wastewaters contain considerable quantities of whey and milk ingredients such as casein, lactose, fat, inorganic salts, detergents and other products for system cleaning [1]. Wastewater is additionally strained by alternating presence of acids or bases which are required for the process of the system cleaning. This fact causes large variations in pH values [2]. Furthermore, the dairy industry wastewater is characterized by large fluctuations in flow as a result of discontinuities present in the production process of various products.

All these aspects increase the complexity of dairy industry wastewater treatment. The most frequently used methods of dairy industry wastewater treatment have been the method of dilution in a natural receiver of wastewater, irrigation of the abandoned land, treatment of septic tanks, biological filtering in the filter filled with slag, gravel or sand, or chemical deposition using chemical coagulants [2-6], and treatment in constructed wetlands and intermittent sand filters [7].

Zeolites have been introduced to the process purification of drinking water and wastewater due to their large specific surface area and the selective adsorption of substances, such as ammonia, dissolved organic matter and many other cations [8]. Moreover, zeolites have advantageous hydraulic pro-
properties, *i.e.*, the filtration capacity for large quantities of water. Compared with other adsorbents, zeolites are more stable, have better filter features, accessible and relatively cheaper [9]. The selling price of natural zeolite, depending on the grain size and type of applied processing procedure, is approximately 0.05-0.20 Euro/kg [10], while the activated carbon rates between 2.5 and 6.0 Euro/kg [11].

Based on numerous studies [8,12-22], it can be concluded that zeolites have great potential as effective adsorbents in numerous processes of purification of drinking water and wastewater, such as water softening, removal of phosphate [8,12-15], the removal of ammonia (from municipal wastewater, wastewater from livestock farms, the barn manure, water from ponds and swimming pools) [12,14-15], the removal of nitrogen [12,14-16], the removal of dissolved organic matter [12,16-19] and color [12,20], the removal of heavy metals (from natural water, acid mine water, industrial wastewater) [12,21-22], the removal of radioactive substances from wastewater [12], desalination seawater [12] and many others.

Natural zeolites perform as polyfunctional sorbents in the wastewater treatment process and they bind a number of harmful components. However, they do not possess the ability of anions adsorption due to negative charge of their aluminosilicate network. Superficial modification of zeolites, by means of organic modifiers, allows partial neutralization of the negative charge of the external surface of zeolite minerals. This process produces organo-zeolite, an adsorbent with increased potential for anion adsorption [23-25] and, what is more important, with ability of simultaneous adsorption of some cationic and organic contaminants [25-26]. Numerous options exist to modify surface of minerals, and they provide a solid basis for further investigation of potential adsorption of other significant pollutants [25,27]. The selling price of organo-zeolite is slightly higher those of natural zeolites. The price was approximately 0.3 euros/kg [11].

This study investigates the probable effects of adsorbents based on organo-zeolites applied in dairy industry wastewater treatment process. The initial hypothesis suggests that the greater coarseness of the adsorbent particles results in higher filtration capacity, but also in lower efficiency in pollutant adsorption capacity. In order to verify this hypothesis, laboratory tests have been organized in a pilot plant containing three filter columns with diverse zeolite granulometry. This research aims to:

- Determine the hydraulic properties of the filter, formed by a column of organo-zeolite, as a function of its granulometric composition and physical characteristics of wastewater.
- Determine the reduction capacity of basic pollutants from the dairy industry wastewater (COD, NH₄⁺, NO₃⁻, and PO₄³⁻).

Determined properties are of particular interest for defining the filter's hydraulic and process loads, as well as for verification of the expected filter effects applied in the case of the dairy industry wastewater treatment.

Obtained results should provide a basis for the application procedures of organo-zeolites in wastewater treatment industry and other industries whose wastewaters have similar bio-chemical loads (food industry, slaughterhouses, juice and beverage industry, etc.).

**MATERIALS AND METHODS**

**Dairy wastewater characteristics**

The wastewater from dairy factory "Imlek" was utilized for the purposes of this research. This industrial unit daily supplies City of Belgrade and central Serbia with milk and dairy products. The total annual production of dairy products this facility is approximately 200,000 m³ of milk and it uses about 800,000 m³ of water [11]. Chemical and physical characteristics of wastewater samples taken from "Imlek" factory (Table 1) do not differ significantly from information found in literature [1-2].

**Theoretical part**

Darcy’s law of filtration describes the fluid flow through porous media [28]:

\[ \dot{V} = K J \]  

or

\[ Q = \dot{V} A = K J A \]  

where: \( Q \) - total flow (m³/s), \( \dot{V} \) - Darcy velocity (m²/s), \( K \) - coefficient of filtration (m/s), \( J \) - hydraulic gradient, \( A \) - cross-sectional area of flow (m²).

Darcy’s law applies when flow is laminar. The change from laminar flow at low velocities to turbulent flow at high velocities is usually related to the dimensionless Reynolds number, \( Re \). For flow through porous material, the Reynolds number is expressed as follows [28]:

\[ Re^v = \frac{\dot{V} d_f}{\nu} < 10 \]  

where: \( d_f \) (m) - effective grain diameter of the filter and the grain size of the filter 15%, \( \dot{V} \) - Darcy velo-
city, $\nu$ (m$^2$/s) - kinematic coefficient of viscosity of liquids.

It is noted that the laminar boundary value for the flow of groundwater is much lower ($Re < 10$) [28] compared to the flow in pipes ($Re < 2000$) [29]. The main reason for this is that the expressions for the groundwater does not use pipe diameter, but grains that form the pores.

The literature features a number of mathematical expressions of different authors (Hazen, 1895; Tercagi, 1926; Lindquist, 1933; Kozeny, 1927; Carman, 1956; Chardabellas, 1964; etc.) for calculating the coefficient of filtration. However, the most recent recommended mathematical expression emerges from the gradient of energy line for laminar flow in tubes of small cross section [30]. This equation was originally proposed by Kozeny (1927) and was modified by Carman (1938, 1956) to finally become the Kozeny-Carman equation [31]. The Kozeny-Carman equation is one of the most widely accepted and used derivations of permeability as a function of the characteristics of the medium [30-32]:

$$K = \frac{8.1 \times 10^{-3}}{\nu} \left( \frac{g n^3 d_m^2}{(1-n)} \right) \rho$$

(4)

where: $g$ - gravitational acceleration, $n$ - porosity, $\nu$ - the kinematic viscosity coefficient.

Equation (4) can be simplified by using following values: gravitational acceleration ($g = 9.81$ m/s$^2$), porosity of the coarse sands and small-grained gravel ($n = 30-35\%$), and the kinematic viscosity coefficient of water coming from the water distribution system with temperature $t = 13^\circ$C ($\nu = 0.0125$ cm$^2$/s). The equation then takes the form:

$$K = 50 d_m^2$$

(5)

For practical applications, it is very important to define the hydraulic energy loss for the flow through the filter, depending on the water flow per unit area $q$. 

### Table 1. Physical and chemical characteristics of wastewater AD „Imlek” dairy industry [11]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximally allowable concentration</th>
<th>Maximum value</th>
<th>Average value</th>
<th>Minimum value</th>
<th>Expected value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical characteristics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow, m$^3$/h</td>
<td>-</td>
<td>157.21</td>
<td>80.03</td>
<td>20.00</td>
<td>-</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>30</td>
<td>37.3</td>
<td>23.96</td>
<td>16.9</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>6-9.5</td>
<td>12.5</td>
<td>8.31</td>
<td>1.61</td>
<td>5-11</td>
</tr>
<tr>
<td>Colloid matted, mg/l</td>
<td>-</td>
<td>4220</td>
<td>1740</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Total solids, mg/l</td>
<td>-</td>
<td>8960</td>
<td>3453</td>
<td>123</td>
<td>1500-5100</td>
</tr>
<tr>
<td>Total solids, mg/l, proportion of organic matter</td>
<td>-</td>
<td>86</td>
<td>76</td>
<td>55</td>
<td>-</td>
</tr>
<tr>
<td>Total solids, mg/l, proportion of inorganic matter</td>
<td>-</td>
<td>14</td>
<td>25</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>Total suspended solids, mg/l</td>
<td>-</td>
<td>55</td>
<td>68</td>
<td>88</td>
<td>-</td>
</tr>
<tr>
<td>Total suspended solids, mg/l, proportion of inorganic matter</td>
<td>-</td>
<td>12</td>
<td>24</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>Total suspended solids, mg/l</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100-1000</td>
</tr>
<tr>
<td><strong>Chemical characteristics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOD / mg O$_2$/l</td>
<td>450</td>
<td>13335</td>
<td>1903</td>
<td>115</td>
<td>1200-3750</td>
</tr>
<tr>
<td>BOD$_5$ / mg O$_2$/l</td>
<td>300</td>
<td>5250</td>
<td>1020</td>
<td>82</td>
<td>800-2500</td>
</tr>
<tr>
<td>N - Kjeldahl, mg/l</td>
<td>-</td>
<td>480</td>
<td>123</td>
<td>17</td>
<td>50-150</td>
</tr>
<tr>
<td>NH$_4^+$ - N, mg/l</td>
<td>15</td>
<td>71</td>
<td>17</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>NO$_3^-$ - N, mg/l</td>
<td>50</td>
<td>90</td>
<td>32</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>NO$_2^-$ - N, mg/l</td>
<td>30</td>
<td>1.9</td>
<td>0.74</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Total P, mg/l</td>
<td>10</td>
<td>180</td>
<td>20.02</td>
<td>4.18</td>
<td>10-100</td>
</tr>
<tr>
<td>SO$_4^{2-}$, mg/l</td>
<td>350</td>
<td>954</td>
<td>198</td>
<td>52</td>
<td>-</td>
</tr>
<tr>
<td>Cl$^-$, mg/l</td>
<td>500</td>
<td>563</td>
<td>193</td>
<td>71</td>
<td>-</td>
</tr>
<tr>
<td>Ca$^{2+}$, mg/l</td>
<td>-</td>
<td>425</td>
<td>148</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>HCO$_3^-$, mg/l</td>
<td>-</td>
<td>728</td>
<td>405</td>
<td>390</td>
<td>-</td>
</tr>
<tr>
<td>Total fats and oils, mg/l</td>
<td>40</td>
<td>212</td>
<td>48</td>
<td>12</td>
<td>400-690</td>
</tr>
</tbody>
</table>
\( \text{Based on Eq. (2), a piezometric head gradient is defined:} \)
\[
J = \frac{Q}{KA}
\]
\( (l/s/m^2) \).

The piezometric head gradient \( J_{\Pi} (m/m') \) per unit area \( (m^2) \) and unit length of filter \( (m') \) can be written in the form:
\[
J_{\Pi} = \frac{q}{K}
\]

### Experimental setup

A laboratory pilot plant was designed to examine the potentials and effects of application of adsorbents based on organo-zeolites in wastewater treatment process (Figure 1). The pilot plant consists of a raw water reservoir volume \( V = 1000 \text{ L} \), fat separator, pumping vessel to maintain constant pressure in the column, the filter columns and piezometric head measurement scales.

The grease separator is a four-compartment structure with dimensions 60 cm \( \times \) 20 cm \( \times \) 30 cm. It contains five sections and a chamber for evacuation of separated fats and oils (Figures 1 and 2). Its role is to separate fats and oils from the wastewater prior filtration process. This would prevent potential filter colimation and abrupt reduction of its filtration effects.

The overflow chamber for level control is set on a steel bracket that can alter its length. This results in changing the filter inlet pressure, the slope of piezometric head \( (J_{\Pi}) \) and Darcy velocity \( (D_{\vartheta}) \), and may influence the flow regime, that is, filtration of water through the column.

The total height of the filter column is \( h = 130 \text{ cm} \), diameter \( \Theta = 125 \text{ mm} \), with adsorbent height of 80 cm (Figures 1 and 2). A metal mesh of high per-

---

**Figure 1.** Scheme of laboratory pilot plant. 1. The raw water tank; 2. Fat separator; 3. Fat-separator chamber for stabilization; 4. Fat-separator chamber for extraction of fats and oils; 5. Pumping tank; 6. Overflow chamber to maintain the level; 7. Filtration column; 8. Piezometric hoses P1-P5; 9. Piezometric head measuring scale \( \Pi_1-\Pi_5 \); 10. Adsorbent; 11. Protective mesh; 12. Pump; 13. Line of overflow water; 14. Regulatory valve; 15. The direction of water flow test; 16. Outlet of filtered water; 17. A mechanism for changing the geodetic elevation (height) overflow chamber to maintain the level; 18. Measuring point of piezometric hose P1; 19. Measuring point of piezometric hose P2; 20. Measuring point of piezometric hose P3; 20. Measuring point of piezometric hose P4; 21. Measuring point of piezometric hose P5; \( \Pi_1, \Pi_2, \Pi_3, \Pi_4, \Pi_5 \) - piezometric head sampling locations; \( \Pi \) - piezometric head in the filter column.
meability is positioned at the bottom and on the top of the adsorbent. The metal mesh has a specific task to flush fine particles of the adsorbent. Before raw water discharge, the column was moistened through outlets for filtered water in the direction opposite to water flow through adsorbent in order to displace trapped air particles.

Water from the raw water tank passes through a grease separator and enters the pumping reservoir from which it rises to the overflow chamber in order to preserve the level. Water flows to the filter from the chamber for the level control. Water flow through the pilot plant is operated by regulatory valves. Steady state \( Q_i \) (L/s) is established by adjusting the valve. A flow is considered steady if there is no change in piezometric head in piezometric hose. After the steady state flow through the column is established, the volume of filtered water, \( V_i \) (L), was measured and also the time, \( t_i \) (s), for which the volume of water passed through the filter. Flow \( Q \) (L/s) through the filter was calculated based on these two parameters.

**Media characteristics**

The adsorbent was formed using granular organo-zeolite. The initial used material was Zeolite tuff from the reservoir Beočin, Fruška Gora, Serbia, and as an organic component in the synthesis of organo-zeolite was used quaternary ammonium salt stearin-dimethyl-benzyl ammonium chloride (SDBAC), manufacturer "Hoechst", Germany.

Zeolite samples were prepared by grinding and wet classification procedure. This process isolated four fractions for the purpose of analysis: 0-0.5 mm, 0.5-0.8 mm, 0.8-3.0 mm and 3.0-5.0 mm. Samples were thermally treated at temperature of 100 °C for 2 h. Subsequently, 0.5 kg of prepared samples were added to 0.5 L SDBAH solutions with concentrations of 50, 75, 100 and 150 mmol SDBAH/L heated at a temperature of 80 °C. The suspensions were filtered after 30 min; precipitates were washed with distilled water and dried at a temperature of 70 °C. The altered cation content and equilibrium concentration of SDBAH were measured in the filtrate. The extent of adsorbed organic components was determined as the difference between the amount of added SDBAH and residual cations in the filtrate after adsorption. The best ratio of the quantity of organic components and zeolite in the synthesis of organo-zeolite adsorbents for the realization of adsorbents as a filter for wastewater treatment has been defined. Based on the results, it varies in range between 50 and 75 mmol M+/kg. Furthermore, the effects of additional factors (grain size, solids content and temperature) on the adsorption of organic compounds on the surface of zeolite were also studied under laboratory conditions, and the results of these tests will be presented in a separate paper. Synthesized organo-zeolites were separated in four fractions (fractions of 0.2 to 2 mm, 2-3 mm, 3-5 mm and 5-7 mm), and three adsorbents were formed. Their particle size distribution is shown in Table 2.

Based on the regular classification by Atterberg, following adsorbents were used during testing: adsorbent I (the most common large fraction), adsorbent II (all fractions evenly distributed), adsorbent III (the most common small fraction), corresponding to mineral mixtures that fall mostly into the category of large sand (0.2 to 2 mm) and fine gravel (2-6 mm) according to Atterberg or by the USDA (U.S. Department of Agriculture) [33].

**Physicochemical parameters determination**

In order to determine the hydraulic characteristics of the formed filter, through the filter column were
discharged tap water (unpolluted water) and twice the wastewater from the dairy industry.

During the filter column operation with a flow $Q_i$, piezometric heads were read ($\Pi_1$, $\Pi_2$, $\Pi_3$, $\Pi_4$, and $\Pi_5$) in the measurement points in the column on which piezometric hoses were installed. Measured data were used to calculate the experimental performance, which is important for understanding the flow regime and water filtration through a column (if the flow is laminar, transitional or turbulent). The Reynolds number, $Re$ (Eq. (3)), Darcy's coefficient of filtration, $k$ (dm/s) (Eq. (4)), and resistance coefficient $\lambda$ are calculated.

To determine the effects of reduction of the basic parameters from dairy industry wastewater in the process of filtration through a column of organo-zeolite, physical-chemical parameters of wastewater were measured using a SECOM PASTEL UV analyzer that works on the basis of UV adsorption spectrophotometry. The SECOM PASTEL UV uses UV imprint characteristic for different pollutants or specific compounds in the sample for estimation of total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), nitrate and anionic surfactants.

For each test series, the water temperature $t$ ($°C$) was measured at the entrance and outlet from the column.

**RESULTS AND DISCUSSION**

**Determination of filtration coefficient**

Table 3 shows the results of measurements performed when filtering “clean” water as a reference point to calculate the coefficient of filtration.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Number of tests</th>
<th>Number of measured piezometric heads</th>
<th>Average Reynolds number ($Re$)</th>
<th>Average coefficient of filtration, $Ksr$ / cm s$^{-1}$</th>
<th>Standard deviation $\sigma$ / cm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent I (def = 2.2 mm)</td>
<td>32</td>
<td>160</td>
<td>9.04</td>
<td>2.37</td>
<td>0.0050</td>
</tr>
<tr>
<td>Adsorbent II (def = 1.6 mm)</td>
<td>31</td>
<td>155</td>
<td>6.05</td>
<td>1.31</td>
<td>0.0019</td>
</tr>
<tr>
<td>Adsorbent III (def = 1.45 mm)</td>
<td>36</td>
<td>180</td>
<td>6.14</td>
<td>1.01</td>
<td>0.0026</td>
</tr>
</tbody>
</table>

The minimal homogeneity of the obtained results (the maximum standard deviation, $\sigma$) occurred in adsorbent I (the most common large fraction), while the maximal homogeneity (the minimal standard deviation, $\sigma$) occurred in adsorbent II (all fractions evenly distributed). This is explained by the fact that in adsorbent I, the flow is on the bounds of laminar flow ($Re > 9$), and this is a condition for the application of Darcy’s equation. In case of other adsorbents, the flow is laminar ($Re \approx 6$).

Comparing the measured data for the filtration coefficient with calculated values from the equation given above, we learn that the obtained data is surprisingly similar. For the adsorbent I (def = 2.2 mm) the measured value was $Ksr = 2.37$ cm/s, while Kozeny’s formula gives $K = 2.42$ cm/s. Adsorbent II (def = 1.6 mm) measured value was $Ksr = 1.31$ cm/s, while Kozeny’s formula gives $K = 1.28$ cm/s. Finally, adsorbent III (def = 1.45 mm) measured value was $Ksr = 1.01$ cm/s, while Kozeny’s formula gives $K = 1.05$ cm/s.

Based on the results of research conducted in 99 experiments (different flows and length of measurement times) with a total of 495 measurements of piezometric heads, it can be concluded that the calculation of the coefficient of filtration, $K$ (m/s), in these filters, the Kozeny equation can be used with sufficient accuracy.

Based on the measured results for the filtration coefficients for three different filters, ratio can be defined between the gradient of piezometric head, $J''$, per unit length of filter ($m/m'$) and flow $q$ per m$^2$ filter ($l/s/m^2$) (Eq. (7)): Adsorbent I ($d_{ad} = 2.20$ mm, $Ksr = 2.37$ cm/s) $J'' = q/23.7$
Adsorbent II \((d_{ef} = 1.60 \text{ mm}, K_r = 1.31 \text{ cm/s})\)

\[ J_{II} = \frac{q}{13.1} \]

Adsorbent III \((d_{ef} = 1.45 \text{ mm}, K_r = 1.01 \text{ cm/s})\)

\[ J_{III} = \frac{q}{10.1} \]

Figure 3 shows the functional dependence of the piezometric gradient elevation \(J_\Pi\) (hydraulic loss) and the discharge of wastewater per \(m^2\).

The results obtained by measurements of filtering wastewater from dairy industry indicate increased filtration coefficient of 50-80%. This is explained by the increase in the coefficient of kinematic viscosity \(\nu\) in wastewater. In practice, the relevant values of hydraulic properties of the filter could be corrected by the linear relation of viscosity coefficient of “pure” water temperature with specific viscosity of “grey” water with the same temperature under investigation [11]. However, additional research must be conducted for the final conclusion.

**Filtration effects on the physical and chemical parameters of wastewater**

Table 4 shows the results of purification of wastewater through the test filters with organo-zeolite. MAC marks the maximum allowable concentration parameter according to the Ordinance on the technical and sanitary requirements for discharge of wastewater into the city sewer [34].

According to Table 4, all analyzed parameters, except for pH values, present increased filtration effects on reduction of pollutants concentration in entering wastewater. The most beneficial effect, that is the greatest reduction in pollutant concentrations, occurs in case of filtration of wastewater through the adsorbent III (the most common small fraction) whose \(d_{ef} = 1.45 \text{ mm}\).

The reduction of organic matter, expressed as COD, ranges from 30 to 50%. This manifestation is explained by the fact that the organic mineral, acting as adsorbent, possesses abilities, in addition to anion adsorption, for simultaneous adsorption of certain ionic and organic contaminants.

Based on the results of the filter length \(L_f = 0.8 \text{ m}\), we calculate the effects of COD reduction by filtration through 1 m’ of the filter.

\[
\Delta COD = \frac{COD_{in} - COD_{out}}{L_f} \quad (\text{mg O}_2/\text{l}/\text{m'})
\]  

For filters AI \((d_{ef} = 2.2 \text{ mm})\), AII \((d_{ef} = 1.6 \text{ mm})\) and AIII \((d_{ef} = 1.45 \text{ mm})\), the following effects of reduction of COD per m’ were obtained: 988, 1480 and 1750 mg O_2/l/m’, respectively. Based on the results, the graph that indicates the filter effects on the COD according to its level and granulometric composition has been formed (Figure 4).

Significant effects of reduction of nitrate nitrogen \((\text{NO}_3^-)\) from 50 to 70% and the effects of adsorption of phosphorus \((\text{PO}_4^{3-})\) of 20% are explained by the adsorption of anionic surfactants, partially neutralized the negative charge of external surface of zeolite, which increases the adsorption capacity organic-mineral anions.

Minor effects of adsorption of ammonia nitrogen \((\text{NH}_4^+)\), when passed through a filter organo-zeolite, is explained by the negative charge neutralization of the...
external surface of zeolite minerals in the formation of organo-zeolite. The negative charge of the natural zeolite used for binding of quaternary ammonium salts (SDBAC) to form organo-zeolite and the adsorption ability of zeolite to NH\textsubscript{4}\textsuperscript{+} is much smaller compared with adsorption capacity of natural zeolites.

The analyzed results show a good effect of adsorption of modified zeolite, since its utilization as a filter for dairy industry wastewater treatment process, caused a positive improvement of the concentration of organic matter expressed by COD, nitrate and ammonium nitrogen in inlet void was low, lower than allowed, and this should be considered when analyzing the results. Obtained results are consistent with the current findings of the researchers in this scientific domain [12-23].

Given the positive effects of the removal of organic matter (expressed as COD), nitrate nitrogen (NO\textsubscript{3}\textsuperscript{-}) and phosphorus (PO\textsubscript{4}\textsuperscript{3-}), the application of filters with an infill of organo-zeolites in dairy industry wastewater treatment can be justified. Further research towards the improvement of phosphorus removal could enhance the system efficiency. For this, P-binding materials, e.g., bauxite, which showed good properties concerning the retention of phosphorus for similar filter granular composition [16], could be investigated to be used alone or even in combination with zeolites for simultaneous removal of organic matter, nitrogen and phosphorous constituents.

Minor effects of adsorption of ammonia nitrogen, as well as low pH value in waste water, which is slightly changed after the filtration, suggest that reactive modified zeolite filters should not be used solely for the treatment of dairy industry wastewater, but in

---

**Table 4. Results of treatment of wastewater through the filter of organo-zeolite**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Wastewater</th>
<th>Adsorbent I, d\textsubscript{w} = 2.2 mm</th>
<th>Adsorbent II, d\textsubscript{w} = 1.6 mm</th>
<th>Adsorbent III, d\textsubscript{w} = 1.45 mm</th>
<th>Maximally allowable discharge concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Inflow</td>
<td>Outflow</td>
<td>%</td>
<td>Outflow</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>4.3</td>
<td>4.4</td>
<td>-</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>COD</td>
<td>2676</td>
<td>1885</td>
<td>29.55</td>
<td>1494</td>
<td>44.18</td>
</tr>
<tr>
<td>NH\textsubscript{4}\textsuperscript{+} - N</td>
<td>5.9</td>
<td>5.5</td>
<td>6.78</td>
<td>5.1</td>
<td>13.56</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-} - N</td>
<td>15.7</td>
<td>7.9</td>
<td>49.68</td>
<td>6.8</td>
<td>56.69</td>
</tr>
<tr>
<td>PO\textsubscript{4}\textsuperscript{3-}</td>
<td>19.1</td>
<td>17.9</td>
<td>6.28</td>
<td>17.4</td>
<td>8.90</td>
</tr>
</tbody>
</table>

**Figure 4. Effects of filtering column height on the reduction of COD.**
combination with reactive filters of natural zeolites and other technologies for dairy industry wastewater treatment. However, this statement requires further investigation of this issue.

CONCLUSION

Experimental studies have confirmed the initial hypothesis in the area of hydraulic properties of the organo-zeolite filter and possible effects on reduction in concentration of key parameters.

The obtained results indicate that the Kozeny equation can be used to calculate the filtration coefficient \( K \) (m/s) in these filters. The loss of hydraulic energy for flow through the filter has been defined, depending on the flow of water per unit area, for filters of different particle size distribution and height.

Moreover, it can be concluded that in all analyzed parameters, except for \( \text{pH} \) values, positive effects of filtration were observed, in terms of reduction in concentration of pollutants in relation to the incoming raw water. This is particularly valid for organic matter expressed as COD (adsorption efficiency of fine-grained filter organo-zeolite AIII approximately 50%), nitrate nitrogen (adsorption efficiency of fine-grained filter organo-zeolite AIII by 70%) and phosphate (adsorption efficiency of fine-grained filter organo-zeolite AIII about 20%).

Based on the overall results of the filtering effects of dairy industry wastewater, and taking into account the filtration characteristics and effects of reduction of physical-chemical parameters of wastewater, \( d_{50} \approx 1.5 \text{ mm organo-zeolite grain size filters} \) are recommended, which need to be combined with reactive filters of natural zeolites and other technologies for dairy industry wastewater treatment.

Acknowledgement

The paper is a part of the research done within the project TR 37018 and TR 37003. The authors would like to thank to the Ministry of Education and Science, Republic of Serbia.

REFERENCES

EFFECTS OF REACTIVE FILTERS BASED ON MODIFIED ZEOLITE... CI&CEQ 19 (4) 583–592 (2013)

[29] D. Stephenson, Developments in water science 6: Pipeline design for water engineers, Estelier, New York, 1976
[34] Official Gazette of the City of Belgrade, 1986.