This paper investigates the effects of several parameters (amount of organic matter, grain size, content of solid phase, stirring rate, and temperature) on the adsorption of stearyl dimethyl benzyl ammonium chloride (SDBAC) in natural zeolite tuff in the process of formation of adsorbents based on organo-zeolite, a potential filter in wastewater treatment process. The obtained results show that the most favorable ratio between the amount of SDBAC and zeolites is 50-75 mmol M+ /kg. Larger grains have lower zeolite adsorption power of organic cations on the surface of zeolite, while favorable percentage of content of solids in the zeolite suspension is 10-20%. Interference between adsorption of mixture and temperature, especially in volumes of SDBAC lower than 75 mmol M+ /kg of zeolite, has no significant impact on adsorption of organic cations on the surface of the zeolite. The obtained results present an initial step for defining the optimal operating parameters for forming adsorbents based on organo-zeolite as a potential filter in wastewater treatment.

Keywords: organo-zeolite, surface active substances, adsorption, filtration.
with a long chain of organic cations, surfactants, thereby building up organic-mineral complexes. The obtained complex is hydrophobic. This allows the adsorption of nonpolar and weakly polar organic pollutants that could not be adsorbed by the natural zeolite [2].

Quaternary ammonium salts are commonly used for surface modification of clay minerals and zeolites [3]. At lower concentrations, organic cations in solution exist in form of monomers, whereas at higher concentrations, in some cases, it leads to the formation of micelles or some type of bilayer. The concentration at which micelles are formed is called the critical micelle concentration (CMC) [4].

Quaternary amine adsorption of clay minerals and zeolite depends on their functional properties (surface charge, cation exchange capacity and exchangeable cation species and the flexibility of the layers). The mechanism of adsorption of quaternary amines on the surface of the zeolites depends on, among other things, the concentration of amine in solution and the ratio of amines to the external cation exchange capacity of zeolite (ECEC). At concentrations lower than the external cation exchange capacity (ECEC), organic cation is linked to the surface of zeolite by electrostatic interactions with the negatively charged surface, whereas at higher concentrations of organic cations (ECEC), leads to the formation of a bilayer, with the second layer binding through hydrophobic interactions to the first [5]. The initial part of the second layer is available for changing the anion [6]. This effect generates an adsorbent with higher adsorption ability of anions, but it is very important that this adsorbent has the capability of simultaneous adsorption of some cationic and organic contaminants. The adsorption of pollutants depends on the properties of adsorbent, such as crystal structure, net charge and charge distribution, the availability of surface, and the properties of the pollutant itself. Numerous options exist to modify surface of minerals, and they provide a solid basis for further investigation of potential adsorption of other significant pollutants.

Formation of organo-mineral adsorbents, as a potential filter for water and wastewater treatment process, depends on several important factors. In addition to the factors affecting the cost of obtaining organo-mineral adsorbents, mainly the amount of organic matter and content of the solid phase, the special significance have the factors that influence the potential application of adsorbents organo-mineral as a filter for water and wastewater treatment, especially the grain size.

With the increase of solid phase content, in terms of adsorption, the number of contacts between the organic modifier and the active centres on the surface of clinoptilolite is increased also. From an economic perspective, it reduces the organo-zeolite drying costs, thereby significantly reducing the costs of production. For potential application of adsorbents as an organo-mineral filter in water and wastewater treatment process, the grain size is a very important feature since the decreased grain size reduces the filtering capacity of adsorbent, and thereby the possibility of its application as a filter.

The research presented in this paper examines the effects of surface adsorption of active substance quaternary ammonium salt stearyl dimethyl benzyl ammonium chloride (SDBAC) in the process of obtaining organo-zeolite depending on various parameters (amount of organic matter, grains size, content of solid phase, stirring speed, and temperature). The main objective is to define the optimal parameters for obtaining surface modified zeolite that will be used as a filter in wastewater treatment, primarily for the adsorption of organic pollutants present in the water. It should be noted that the effects of various parameters are studied separately, and the best combination of parameters to obtain surface-modified zeolite is not analyzed. Such an analysis requires more extensive research and certainly will be the subject of further interest by the author.

The obtained organo-zeolite has the ability to adsorb nonpolar and weakly polar organic pollutants, while the larger amounts of adsorbed SDBAC on the surface of zeolite does not indicate better adsorption characteristics of zeolite. Hydraulic characteristics of the filter formed of organo-zeolite and reduction efficiency of basic parameters of wastewater in the filtering process of organo-zeolites with different granulometric composition, will be presented in a separate paper. The verification of the obtained adsorption capacity of modified zeolite in elimination of nonpolar and weakly polar organic pollutants will be analyzed in the future.

**EXPERIMENTAL**

**Materials**

Adsorbent is formed using granular organo-zeolite. The initial used material was zeolite tuff from the reservoir Beočin, Fruška Gora, Serbia. As an organic component in the synthesis of organo-zeolite, quaternary ammonium salt stearyldimethylbenzyl ammonium chloride (SDBAC) was used (Hoechst, Germany).
Zeolite samples were prepared by grinding and wet classification procedure. This process isolated four fractions for the purpose of analysis: sample Z-I (fraction 0.0–0.5 mm), sample Z-II (fraction 0.4–0.8 mm), sample Z-III (fraction 0.8–3.0 mm) and sample Z-IV (fraction 3.0–5.0 mm). Subsequently, 0.5 kg of the starting zeolite and the zeolite thermally treated at temperature of 100 °C for 2 h, were added to 500 ml SDBAC solutions with concentrations of 50, 75, 100 and 150 mmol SDBAC/l heated at a temperature of 25 or 80 °C. The suspensions were filtered after 30 minutes; precipitates were washed with distilled water and dried at a temperature of 70 °C. The altered cation content and equilibrium concentration of SDBAC were measured in the filtrate. The extent of adsorbed organic components was determined as the difference between the amount of added SDBAC and residual cations in the filtrate after adsorption. These samples were tested on influence of laboratory conditions on adsorption of organic components on the surface of zeolites. The adsorption experiments were performed at room temperature.

**Adsorption experiments**

Amounts of organic substances required for the surface modification of zeolite were studied by means of adsorption experiments, so that the added amount of organic substances gives the following relations of adsorption experiments, so that the added amount of organic substances gives the following relations $ECEC$ (mmol M+/kg sample)/SDBAC (mmol M+/kg sample): 1:0.33, 1:0.67, 1:1, 1:1.33, 1:2, 1:2.67 and 1:4.

The effects of grain size on adsorption of SDBAC on the zeolite were investigated by monitoring the kinetics of SDBAC adsorption on the surface of formed samples Z-I to Z-IV.

The effects of the solid phase on SDBAC adsorption were investigated using following method: adsorption mixtures, containing the solid phase of 5, 10 and 20%, were mixed at a speed of 2000 rpm at a given time, while the kinetics of adsorption on the surface of clinoptilolite SDBAC was monitored.

The effect of mixing intensity on the adsorption SDBAC was studied by the adsorption kinetics followed by SDBAC on the surface of zeolite fraction 0.4–0.8 mm (20% concentration of suspension) at the following rates of mixing: 1500, 2000, 2500 and 4000 rpm. For comparison, an experiment was performed and adsorption measured without interference with adsorption of the mixture.

Temperature effects on SDBAC adsorption were investigated by adding the initial sample at 25 °C (labeled HZ) and thermally processed zeolite sample at 100 °C (TZ), to reduce the moisture content pre-sent on the surface, the quaternary ammonium salt solutions SDBAC whose temperature was 25 (HR) and 80 °C (TR). Four combinations of suspensions with different SDBAC concentrations were prepared (50, 75, 100 and 150 mmolM+/kg of zeolite): HZ (25 °C) - HR (25 °C), TZ (100 °C) - HR (25 °C), HZ (25 °C) - TR (80 °C), and TZ (100 °C) - TR (80 °C). After 30 min of interaction, the samples were filtered and the contents of altered cations and the balance concentrations of organic cations in filtrates were determined.

**Methods for determining characteristics of zeolites and organo-zeolite**

The initial samples of zeolite and obtained organo-zeolites were characterized using the following methods: determination of chemical composition and mineral compositions, determination of total cations exchange capacity (CEC), the external cations exchange capacity (ECEC) and free amine in solution (SDBAC).

Quantitative chemical analysis of the initial zeolite samples for determination of chemical composition was performed on a Perkin Elmer 703 atomic adsorption spectrophotometer after the destruction of the sample by melting.

The mineralogical composition of the initial zeolite samples was determined by a Philips PW-1710 X-ray diffraction diffractometer with a Cu anticathode and graphite mono-chromator. The sample was recorded in the range of angles 2θ between 4 and 65°, with a time constant of 0.25 s and a step of 0.02°.

The total cation exchange capacity of initial zeolite sample with different grain size was determined by the standard method of ion exchange with ammonium chloride [7]. The mass of 1 g sample was left to stand for 24 h in 100 ml of ammonia solution, at pH 7, with occasional shaking. After completion of ion exchange, the suspension is filtered and the concentration of exchangeable Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$ was determined in the filtrate, whose sum calculated per kg of sample is total $CEC$. The concentrations of Ca$^{2+}$ and Mg$^{2+}$ were determined by titration with standard EDTA solution. The concentrations of Na$^+$ and K$^+$ were determined by a flame photometer (Dr Lange Flammen-Photometer M&D - Propane).

The external cation exchange capacity of zeolites initial sample with different grain sizes was determined by the method of Ming and Dixon [8], and modified by Bowman [6].

The method of titration with a standardized solution of Na-lauryl sulfate was used to determine the free amines in solution that were not adsorbed on the...
RESULTS AND DISCUSSION

Characteristics of the initial sample of zeolite

Quantitative chemical analysis revealed that the basic sample of zeolite contains 66.87% SiO₂, 13.46% Al₂O₃, 8.12% of other oxides (Fe₂O₃, CaO, MgO, Na₂O and K₂O), while the annealing loss (loss of ignition) was 11.45%.

XRPD analysis of the initial sample was used to obtain the zeolite powder diffraction. Based on this, it can be concluded that the dominant phase is a present mineral clinoptilolite, while other accompanying minerals are quartz, feldspar and carbonate. Semi-quantitative X-ray analysis of multiphase samples showed that the mineral clinoptilolite is present in range between 75 and 80%.

The type and content of exchangeable cations in the initial zeolite samples of different fractions are shown in Table 1. The total cation exchange capacity was obtained by adding the contents of exchangeable cations.

Impact of SDBAC amount on the formation of organically modified zeolite

When it comes to the effects of the amount of added organic substance SDBAC on its adsorption on zeolites, the obtained results show a linear dependence of the adsorbed amount relative to the added amount of organic substance SDBAC up to the amount of added organic substance SDBAC of 150 mmol M⁺/kg (ECEC/SDBAC ratio 1:2). Also, for all added amounts of organic substance SDBAC, linear dependence of the percentage of adsorbed amounts relative to the amount of added organic substance SDBAC was observed.

For the added quantity of organic substance SDBAC of 25 mmol M⁺/kg (ECEC/SDBAC ratio 1:0.33) the total amount added organic substance, or 100%, was adsorbed. However, for added quantities of organic substance SDBAC of 50, 75 and 100 mmol M⁺/kg (ECEC/SDBAC ratio 1:0.67, 1:1.33 and 1:1), the following amounts were adsorbed: 45, 65 and 80 mmol M⁺/kg or 90.0, 86.7 and 80.0% of added organic substance, respectively. For added quantities of organic substance SDBAC of 150 and 200 mmol M⁺/kg (ECEC/SDBAC ratio 1:2 and 1:2.67), the maximum amount of 105 mmol M⁺/kg, that is 70 and 52.5% of added organic substance were adsorbed. For the added quantity of organic substance SDBAC of 300 mmol M⁺/kg (ECEC/SDBAC ratio 1:4), and the adsorbed amount decreased to 90 mmol M⁺/kg, or 30% of added organic substance.

The maximum value of SDBAC adsorption in the zeolite sample is 105 mmol M⁺/kg and it exceeds the value of external capacity of clinoptilolite, while for the tested samples is Z-IV (fraction 3.0–5.0 mm) ECEC = 73 mmol M⁺/kg, Z-III (fraction 0.8-3.0 mm) and Z-II (fraction 0.4-0.8 mm) ECEC = 75 mmol M⁺/kg, Z-I (fraction 0.0-0.5 mm) ECEC = 78 mmol M⁺/kg (Table 1). This result confirmed the information presented in the literature indicating that the adsorption of SDBAC takes place through several mechanisms, not only through the mechanism of cation exchange [10]. Two major mechanisms are generally proposed for the adsorption of cationic surfactants onto different clays and zeolite minerals are ion exchange and hydrophobic interactions [11,12].

Since the maximum value of SDBAC adsorption in the sample is 105 mmol M⁺/kg and it exceeds the value of external capacity of clinoptilolite, the recommend ratio of SDBAC and zeolite is in the range of 50–75 mmol M⁺/kg zeolite (ECEC/SDBAC ratio 1:0.67-1:1).

Figures 1 and 2 present results of the effect of grain size on SDBAC adsorption on zeolites.

The results shown in Figure 1 indicate that the increase in grain size reduces the adsorption of organic cations on the surface of clinoptilolite, which is not reflected in the size of the 75 SDBAC mmol M⁺/kg. When the amount of added SDBAC is less than 75 mmol M⁺/kg in the samples of zeolites with smaller grains Z-I (fraction 0-0.5 mm) and Z-II (fraction 0.4-0.8 mm, the adsorption SDBAC is complete (the index of adsorption 100%), while the samples with larger grains Z-III (fraction 0.8-3.0mm) adsorption index of about 90%, and Z-IV (fraction 3.0-5.0 mm) about 80%. The difference is especially noticeable at higher added concentrations of SDBAC (greater than 100 mmol M⁺/kg of zeolite). For the amount of added...
150 mmol M⁺/kg SDBAC of zeolite index adsorption SDBAC in a sample of zeolite Z-I (fraction 0-0.5 mm) was 90% (135 mmol M⁺/kg sample) in contrast to the sample Z-IV (fraction 3.0-5.0 mm), where the adsorption index was 57% (86 mmol M⁺/kg sample).

The results shown in Figures 1 and 2 present equivalent ionic exchange between the exchangeable cations in the zeolite and SDBAC in the case of Z-I samples (fraction 0.4-0.8 mm) when the amine is added in a quantity equal to or less than the ECEC value. Also, the sum of cations, changed at different amounts of added amines, does not exceed the ECEC value of the zeolite. For Z-III (fraction 0.8-3.0 mm) and Z-IV (fraction 3.0-5.0 mm) samples change with organic cations are not equivalent. Although the adsorbed SDBAH value is equal to or greater than the value ECEC zeolite cations, the content of the filtrate is significantly smaller than the zeolite samples with smaller grain size distribution. The obtained results indicate that the increase in grain size of zeolite reduces the availability of exchangeable cations in the reaction of ion exchange with organic cations.

Figure 3 shows the value of adsorbed amount of organic cations as a function of time for different filings of the solid phase. From the perspective of adsorption, the number of contacts between the organic modifier and the active centers on the surface of clinoptilolite increases with the increased content of the solid phase. Adsorption rate is proportional to the total amount of active centers on the surface of clinoptilolite.

Figure 3 shows that the maximum rates of adsorption occur in the first 5 min of mixing, while the suspensions containing 5, 10 and 20% of solid phase adsorb close to 20, 35 and 50% of the initial amount.
of added organic cations, respectively. The rate of adsorption in the first 5 min of mixing is the highest for the suspension containing 20% of solid phase, while nearly 50% of the initial volume of added organic cations is adsorbed. This can be explained by the fact that the suspension containing 20% of solid phase has the largest contact frequency of organic cation and active centers on the surface of zeolite.

The adsorption rate rapidly decreases subsequently due to the reduced number of active centres available for adsorption and, after 30 minutes, it is practically equal for all three suspensions with different content of the solid phase.

In suspensions containing 20% of solid phase majority of the quantity of organic cations (95%) is adsorbed in 90 min, while in the suspensions containing 5 and 10% of the solid phase the equivalent amount of organic cations (91 and 93%) is adsorbed in 120 min. If a suspension contains more than 20% of the solid phase, it is possible to adsorb more than 95% of organic cations, which requires further investigation.

Based on the obtained results, the recommended percentage of solids content in the zeolite suspension is 10–20% with 30–60 min of mixing time.

The amount of adsorbed organic cations on the surface of the zeolite as a function of time at different mixing speeds is shown in Figure 4.

Figure 3. Dependence of SDBAC adsorbed on the zeolite surface of contact time for different rates of solid phases.

Figure 4. Dependence of SDBAC adsorbed on the zeolite surface of contact time for different mixing intensities.
speeds of 2500 and 4000 rpm, after 120 min of adsorption of 95%, or slightly less than 90% organic modifier. As can be seen from Figure 4, the stirring speed has little effect on the amount of adsorbed organic modifier, especially for the mixing times up to 30 min. This is confirmed by the fact that the suspension that is not mixed after 30 min contains identical amounts of adsorbed organic modifier as the suspension mixed at 4000 rpm.

Given the significant influence of grain size of zeolite to the possibility of its application in wastewater treatment, a set of experiments were conducted to investigate the influence of mixing rates on the grain zeolite fragmentation. The obtained results show that the stirring at low speed (1500 rpm) increases the portion of finer fraction (less than 0.4 mm) from 0% in the initial sample to 16%, while the stirring speeds of 2500 rpm and higher, increases this share to 25%, that is, a significant reduction grain size of zeolites occurs. Based on the obtained results, it can be concluded that the stirring rate has no significant influence on the course and speed of adsorption. Moreover, it has no significant influence on the amount of adsorbed organic modifier, but it has a negative effect, especially at high mixing rates, on the significant grain refinement of zeolite.

The amount of adsorbed cations depending on the added amount of SDBAC, for different temperatures, is shown in Figures 5 and 6.

Figure 5 shows that the adsorption of organic cations on the surface of clinoptilolite and the starting amine concentration of 50 mmol M+/kg of zeolite is complete, regardless of the thermal treatment of zeolite and the temperature of the suspension. When the amount of added amine is between 50–75 mmol M+/kg of zeolite the adsorption of organic cations on the surface of the zeolite is nearly complete (greater than 95%) regardless of the suspension temperature. When the SDBAC is added, there is an evident positive effect of temperature on adsorption of organic cations. When the amount of added SDBAC is 75, 100 and 150 mmol M+/kg of zeolite the effect of temperature increases in the series: TZ (100 °C) < TR (80 °C) < TZ (100 °C) + TR (80 °C). In the case of added SDBAC quantities of 75 and 100 mmol/kg of zeolite, the adsorption was complete (100%), and it was necessary to warm the solution of organic salts. The maximum adsorption was 123 mmol M+/kg of sample, added in case quantities of 150 mmol/kg of zeolite in the sample and heating the solution, which is in agreement with literature data [13]. This value exceeds the value of the external cation exchange capacity, and based on basis we can conclude that there is a so-called “double-layer” adsorption.

Figure 6 presents approximately equivalent exchange of inorganic cations with organic cation SDBAC⁺ if the initial amine concentration is 50 mmol/kg of zeolite. In case of added amine in range 75, 100 and 150 mmol M+/kg of zeolite (adsorbed 75, 100 and 123 mmol M+/kg of zeolite in the heating of the sample and the solution of organic salts) content of altered cation was 75, 74 and 72 mmol M+/kg of zeolite. These values of changed inorganic cations are expected since the values are equivalent to the external cation exchange capacity (ECEC). The results confirm the formation of a monolayer on the surface of clinoptilolite mineral based on the cation exchange mechanism. Based on the obtained results it can be concluded that temperature has no significant effect on adsorption of organic cations on the surface of the zeolite if the amounts of added SDBAC is less than 75 mmol M+/kg of zeolite, but the inc-
increased amount of added amine the positive effect of temperature on adsorption of organic cations becomes evident.

CONCLUSION

Based on the results of experimental investigation of the effects of various parameters on the adsorption effects of quaternary ammonium salts stearyl dimethyl benzyl ammonium chloride (SDBAC), in obtaining organo-zeolite adsorbents for the formation of a filter for wastewater treatment, it is found that:

- The most favorable ratio of the quantity SDBAC and zeolite is 50-75 mmol M+/kg.
- Larger grains have lower zeolite adsorption of organic cations on the surface of zeolite.
- The most favorable portion of zeolite solid phase in suspension is ≈10–20%.
- Mixing of the absorption suspension has no significant effect on the amount of adsorbed organic cations on the zeolite surface, especially at higher speeds, but it negatively affects the grain crushing of the zeolite.
- The temperature has no significant effect on adsorption of organic cations on the surface of zeolite in amounts of added SDBAC lower than 75 mmolM+/kg of zeolite, but, with the increasing amount of added amines, the positive effect of temperature becomes evident.

The presented results are a starting point for defining the optimum operating parameters for forming adsorbents based on organo-zeolite as a filter for wastewater treatment.

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REFERENCES

FORMIRANJE MODIFIKOVANIH ZEOLITA KAO FILTARSKE ISPUNE ZA PREČIŠĆAVANJE OTPADNIH VODA

U radu je ispitivan uticaj više parametara (količina organske supstance, veličina zrna, sadržaj čvrste faze, brzina mešanja i temperatura) na adsorpciju stearildimetilbenzil ammonijum-hlorida (SDBAH) na prirodnom zeolitskom tufu, pri formiranju adsorbenata na bazi organo-zeolita kao mogućeg filtra za prečišćavanje otpadnih voda. Rezultati pokazuju da je najpovoljniji odnos količine kvaterlarnog amina i zeolita 50-75 mmol M+/kg. Veća zrna zeolita imaju manju adsorpciju organskog katjona na površini zeolita, a najpovoljniji procenat sadržaja čvrste faze zeolita u supsenziji je 10-20%. Mešanje adsorbicne smeše i temperatura, posebno pri količinama dodate kvaternarne amonijumove soli nižim od 75 mmol M+/kg zeolita, nemaju značajni uticaj na adsorpciju organskog katjona na površini zeolita. Dobije rezultati su polazna osnova za definisanje optimalnih radnih parametara za formiranje adsorbenata na bazi organo-zeolita kao mogućeg filtra za prečišćavanje otpadnih voda.

Ključne reči: organo-zeolit, površinski aktivne substance, adsorpcija, filtracija.