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# Elemental and morphological features of thermally modified clinoptilolite as an efficient sorbent for benzo(a)pyrene extraction from water preceding GC - MS analysis

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## ABSTRACT

Monitoring of benzo(a)pyrene (BaP) levels in water is of great importance because BaP is used as a marker for pollution by other polycyclic aromatic hydrocarbons (PAHs). The elemental and morphological features of clinoptilolite used as a sorbent in dispersive micro-solid phase extraction (D-µ-SPE) of BaP from water samples, before Gas Chromatography - Mass Spectrometry determination (GC - MS) is described.

SEM micrographs demonstrated agglomerated particles of Clinoptilolite with no changes in particles, but with increased porosity for Clinoptilolite modified at 300 and 400 $^{o}$C. The content of elements is lower in thermally modified Clinoptilolite at higher temperatures (300 and 400 $^{o}$C) than for clinoptilolite treated at 120 $^{o}$C. After the extraction, EDX analysis of clinoptilolite adsorbed BaP, showed the increased percentage of carbon in the modification prepared at 300 $^{o}$C, indicating the structure of the applied sorbent is more suitable compared to one treated at 400 $^{o}$C. Recovery values of surrogate standards demonstrate good extraction efficiency for modification at 300 $^{o}$C and 400 $^{o}$C, but cheaper modification (prepared at 300 $^{o}$C) was selected for BaP analysis.

*Keywords*: *SEM, EDX, GC – MS, PAH, Benzo(a)pyrene, Clinoptilolite*

## Introduction

Biogenic and anthropogenic polycyclic aromatic hydrocarbons (PAHs), mainly derived from fossil fuel combustion, incineration, production of coke and asphalt, oil refining, aluminium manufacture, and burning of agricultural and forest biomass fuels, can reach water bodies and contaminate rivers due to storm water runoff and discharges of domestic sewage and industrial effluents (Lima et al., 2015).

Initially, concern about PAHs was only focused on their carcinogenic property (Rubin, 2001). Recently, however, searchlight has been beamed on their antagonism of hormonal functions and their potential effect on reproduction in humans, as well as their ability to depress immune function (Uppstad et al., 2011). These concerns have prompted both the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA). BaP is the only PAHs with enough toxicological evidence to allow the setting of a guideline (Muyela et al., 2012); according to that, BaP is often use as a marker for PAH pollution. At recent times, sorbent-based sample pretreatment techniques are techniques of choice for PAH analysis in water (Ćirić et al., 2018).

In general, usage of natural zeolites has increased for sorbent-based sample pretreatments (Faghihian et al., 2011; Ghazaghi et al., 2015). Most natural zeolites are formed as a result of volcanic activity.

Zeolites are aluminosilicate minerals with rigid anionic frameworks containing well-defined channels and cavities. These cavities contain metal cations, which are exchangeable, or they may also host neutral guest molecules that can also be removed and replaced. Cavities are usually occupied by $H_2O$ molecules. In the hydrated phases, dehydration occurs at temperatures mostly below about 400 °C and is largely reversible. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedra (Coombs et al., 1997).

The majority of natural zeolites have a general formula, $M2/n:Al_2O_3: \times SiO_2:yH_2O$, where M stands for the extra-framework cation (Bogdanov et al., 2009). The mineral structure is based on $AlO_4$ and $SiO_4$ tetrahedra, which can share 1, 2, or 3 oxygen atoms, so there is a wide variety of possible structures as the network is extended in three dimensions. This structural feature determinates their microporous structure.

Based on the pore size and absorption properties, zeolites are among the most important inorganic cation exchangers and they are used in industrial applications for water and waste water treatments, catalysis, nuclear waste, agriculture, animal feed additives, and in biochemical applications (Bogdanov et al., 2009).

The mineral assemblies of the most common zeolite occurrences in nature are clinoptilolite and mordenite-containing tuffs, in which the zeolite clinoptilolite and mordenite content is high (80% and over). It may appear with the aluminium phyllosilicate clay smectite (bentonite) and accompanying phases present in lower percentages cristoballite, calcite, feldspar, and quartz. However, other types of zeolites (*e.g.*, phillipsite, chabazite) and clay minerals may dominate the mineral tuff assemblage, and properties of such materials may vary in the widest sense with respect to the final mineral content (Cejka et al., 2005).

Clinoptilolite belongs to the group heulandite (HEU), which possesses a two - dimensional structure (Roth et al., 2014). HEU tetrahedral framework is formed from tetrahedral

$SiO_4$ and $AlO_4$ units and contains three sets of intersecting channels. Two of the channels are parallel to the c-axis: A channels are formed by strongly compressed ten - membered rings (aperture 3.1 × 7.6 Å) and B channels are confined by eight-membered rings (aperture 3.6 × 4.6 Å). C channels are parallel to the a-axis and they are also formed by eight-membered rings (aperture 2.6 × 4.7 Å). Clinoptilolite unit cells are monoclinic with space group C2/m (Alberti, 1975; Armbrusteret al., 2001; Baerlocher et al., 2007). The general chemical formula is $(Na,K)_6Al_6Si_{30}O_{72}\cdot 20H_2O$ ) (Armbrusteret al., 2001; Tsitsishvili et al., 1992) and the Si/Al ratio of clinoptilolite may vary from 4.0 to 5.3 (Kowalczyk et al., 2006).

Clinoptilolite shares a high structural similarity with the zeolite heulandite (they are 97% isostructural) and it is distinguished from helaundite by a higher silicon to aluminium ratio in favour to silicon, where $Si / Al > 4.0$ and $(Na + K) > (Ca + Sr + Ba)$ (Boles, 1972). The thermal behaviour of clinoptilolite and heulandite is also different. The clinoptilolite structure is still not destroyed after 12 h of heating at 750°C, whereas the heulandite structure is destroyed after 12 h at 450°C (Ghiara et al., 2001).

Zeolites are of high interest to researchers working in the various fields such as energy recovery technology (Xu et al., 2019), water adsorption (Melkon et al., 2018), ion exchangers, adsorbents, catalysts (Auerbach, 2003; Gorshunova et al., 2016), acid-catalyzed dehydration of alcohols (Aleksei et al., 2015; Junko et al., 2005; Seonah et al., 2015) or dry reforming of methane (Alotaibi et al., 2015) and synthesis of zeolites with nonporous titania for corrosion resistance applications (Toshiyuki et al., 2015) as well for agriculture and food production (Nazife et al., 2017), where natural zeolites are used mainly as ion exchangers and in environment remediation (Marantos et al., 2011; Stocker et al., 2017). The majority of studies on clinoptilolite were done by using different, so-called activated materials to increase either the surface area or to improve the clinoptilolite general adsorption or the ion - exchange capacity. Activation may be performed either through chemical treatment, *e.g.*, with an acid, by replacing stabilizing cations, or through mechanical modifications by means of different micronization methods, which may all increase the surface area and change the ion - exchange properties and adsorption capacity (Abdulkerim, 2012; Akimkhan, 2012; Canli et al., 2013b).

**Table 1.** Mineral Composition of Clinoptilolites from several countries

| Composition | Serbia (Milovanović et al., 2015) | Japan (Kumar and Shigeo, 2009) | China (QiuJue et al., 2015) | Greece (Evangelos et al., 2016) | This study (Sekulic et al., 2013) |
|---|---|---|---|---|---|
| $SiO_2$ | 72.20 | 77.96 | 66.45 | 68.25 | 62.28 |
| $Al_2O_3$ | 12.20 | 14.02 | 13.30 | 13.19 | 12.33 |
| $Fe_2O_3$ | 5.70 | 1.30 | 1.49 | 1.41 | 3.20 |
| $TiO_2$ | 0.90 | - | 0.19 | 0.17 | / |
| MgO | 1.0 | 0.46 | 0.92 | 1.14 | 1.18 |
| CaO | 5.0 | 1.23 | 3.97 | 0.75 | 6.65 |
| $Na_2O$ | 0.50 | 1.15 | 1.02 | 4.12 | 1.46 |
| $K_2O$ | 2.50 | 3.88 | 1.54 | 1.66 | 0.85 |

The chemical and thermal treatments are the most used techniques to modify the zeolite's characteristics. These treatments allow 1) the removal of impurities; 2) the enhancement of sorption properties, surface area, and porosity; and also 3) the determination of important crystallinity loss (Akkoca et al., 2013).

The aim of this work is  the characterization of thermally modified clinoptilolite as an efficient sorbent in sample pretreatment preceding Gas Chromatography – Mass Spectrometry (GC – MS) determination of BaP. Prepared clinoptilolite modifications were applied in Dispersive micro-solid phase extraction (D-μ-SPE) to extract BaP from spiked water samples and analyse its content. The elemental and morphological features of used sorbents before and after sample pretreatment are performed using SEM and SEM – EDX techniques.

## Methods and materials

### Chemicals and reagents

Hexane (HPLC grade), Acetonitrile (HPLC grade) - Sigma Aldrich; Surrogate standard mix: 2- chlorphenol-3,4,5,6-$d_4$, 2,4,6-tribromophenol, 2- fluorobiphenol - Supelco, Bellefonte, Pennsylvania; benzo(a)pyrene – Supelco; perylene $d_{12}$ - Bellefonte, Pennsylvania; Deionized water specific conductivity - 0.05 μS cm$^{-1}$.

### Standard solution preparation

As internal standard solution (ISs), was used perylene $d_{12}$ prepared in dichloromethane (10 ppm). Surrogate standard mix solution in concentration of 0.75 ppm was added to every tested model sample in order to monitor extraction efficiency.

A series of standard solutions was prepared by diluting 0 - 200 μl of the standard solution containing BaP in hexane. Each standard solution contained 100 μl of internal standard solution and 100 μl of surrogate standard solution and was prepared in triplicate.

### Preparation of model water samples

Deionized water, with verified absence of BaP, was used to prepare the model water samples which were spiked with BaP at two concentration levels 0.5 and 1.5 ppm. Surrogate standards mix was added in every model water samples in total concentration of 0.75 ppm. Blanks were prepared following the same procedure without adding BaP solution.

### Sorbent preparation

Clinoptilolite (grain size 0.063 - 0.1 mm) containing over 90% clinoptilolite, obtained from the mine Zlatokop (South Serbia), was washed with deionized water to remove impurities, dried and thermally modified in Annealing furnace for 3 h at temperatures of 120 °C , 300 °C, 400 °C (Ćirić et al., 2018). Elemental and morphological features were determined before and after the extraction procedure.

## Dispersive micro-solid phase extraction (D-µ-SPE)

Dispersive micro - solid phase extraction (D-µ-SPE) was used to extract benzo(a)pyrene from model water samples. Hexane was used as the extractant and solvent mixture acetonitrile-water (1:4 v/v) a as disperser -. Model samples (400 µL) containing two levels of BaP concentration 0.5 and 1.5 and surrogate standard mix with total concentration of 0.75 were transferred into microextraction tubes, which contained 460 mg of the tested sorbent. After shaking (1 min) and centrifugation (5 min) water was removed *via* micropipette and 500 µL of extractant and 100 µL of disperser was added to the solid residue. After shaking for 5 min and centrifugation (15 min), 400 µL of extract was transferred to GC vial (Ćirić et al., 2018). Then, 200 µL of internal standard mix was added and extracts were analyzed by gas chromatography - mass spectrometry. All experiments were done in triplicate.

## Gas Chromatography – mass spectrometry

All extracts were analyzed on a 7890/7000B GC-QQQ-MS system (Agilent Technologies, USA) in the selected ion monitoring (SIM) mode.

**Chromatographic separations conditions**: Column (HP-5 MS) - 5% Phenyl Methyl Siloxane column (30 m x 250 µm x 0.25 µm); Temperature program: 75 °C for 3 min, then 6 °C/min to 300 °C, keeping the final temperature for 10 min; Total run time*:* 50.5 min; Injection Volume/mode 2.5 µL of extracts was injected in splitless mode; Carrier gas; Helium with a flow of 1.0 mL/min.

**Mass Spectrometry conditions:** Ionization voltage: 70 eV**;** Acquisition mass range: 40-560**;** Scan time: 0.32 s.

### Scanning Electronic Microscopy (SEM)

Morphological features thermally modified clinoptilolite were examined by scanning electronic microscopy (SEM), model: SEM - JSM 5300 JEOL instrument; Accelerating voltage was 0.5–30 kV, resolution 4.5 nm, magnification × 15–20.000.

### Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX)

Elemental compostition was performed using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) (Phenom-World, The Netherlands), and it was performed before and after extraction of PAHs from water.

## Results and discussion

Characterization of clinoptilolite after heat treatment to 120 $^{o}$C, 300 $^{o}$C and 400 $^{o}$C was done by SEM - EDX methods. The morphological structures of the clinoptilolite were determined by SEM (Figure 1).

From the micrographs, we can observe that the clinoptilolite particles are agglomerated, and there is no drastic changes in the particles shape where lamellar structure and heterogenicity were preserved after thermal modification. The lamellar and heterogenic structure of the modified clinoptilolite is noticed. If we narrow our focus to the samples thermally modified at different temperatures, we can see that clinoptilolite treated at 300 $^{o}$C and 400 $^{o}$C have the higher porosity and cavities than clinoptilolite treated at 120 $^{o}$C. Increased porosity is a result of water loss due the heating.

Most zeolites can be dehydrated without a major change in the crystal structure, followed by their rehydration through water adsorption from the atmosphere or proximate liquid phase

(Cadar et al., 2020). Dehydration reaction affect the thermal expansion or contraction of samples. The high-temperature exposure does not always produce improvement in the surface area and porosity. Recent work (Wahono et al., 2019) has shown that high temperature, above 800 °C, leads to the loss of a porosity. It indicates that the material is converted from porous material into a solid or compact material which destructs the pore (Cobzaru, 2012; Wang and Zhu, 2006). For this reason, modifications were made in areas of lower temperatures.

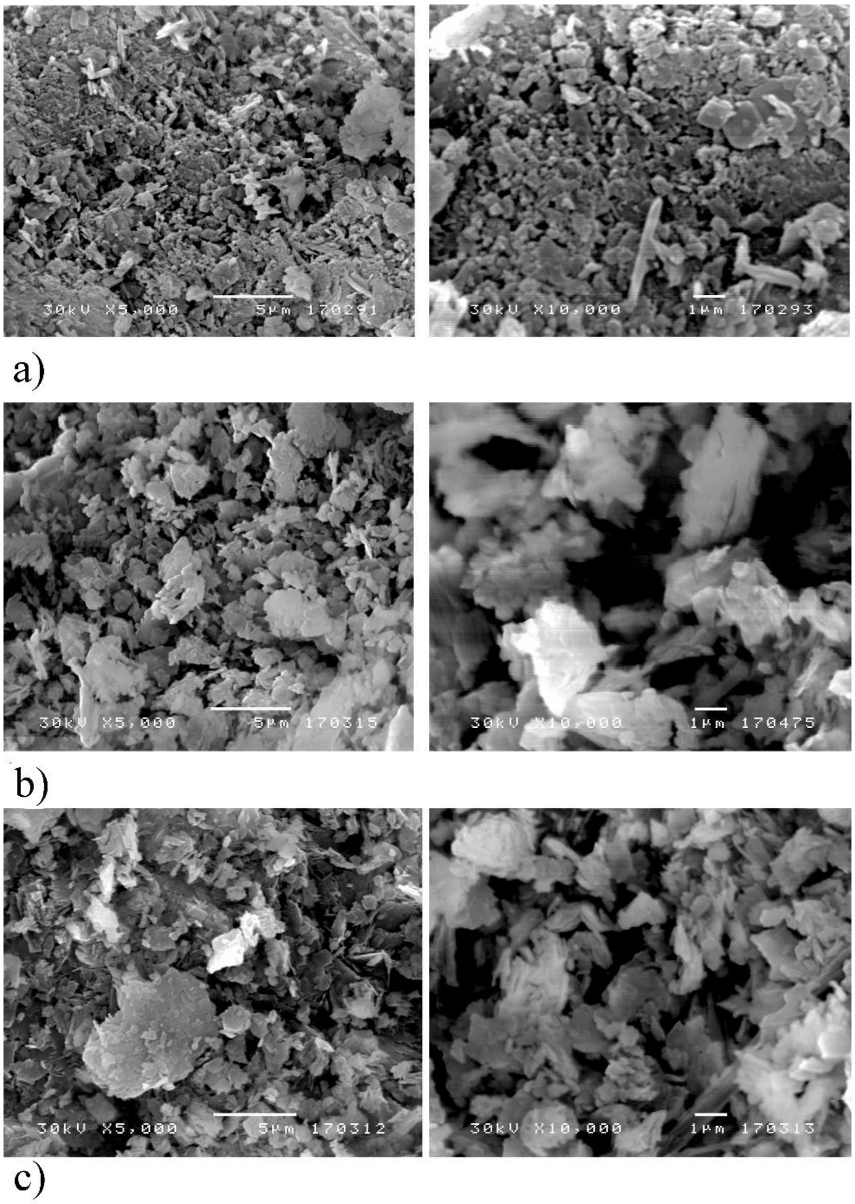
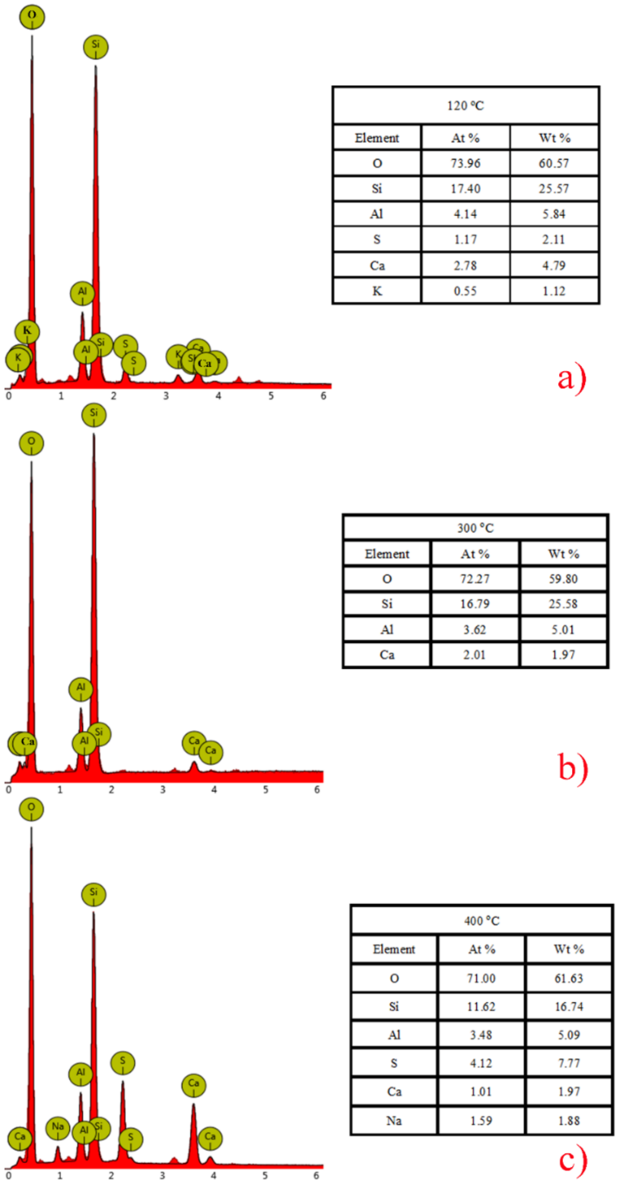


**Figure 1.** SEM morphology of clinoptilolite in various temperature treatments: (a) 120 $^{o}$C; (b) 300 $^{o}$C; (c) 400 $^{o}$C

## EDX analysis

EDX spectra specified the element composition of analyzed samples of clinoptilolite before the extraction procedure and results are presented in Figure 2. Weight (wt %) and atomic percentage (at %) of elements are included within the Figure 2.



| 120 °C | | |
|---|---|---|
| Element | At % | Wt % |
| O | 73.96 | 60.57 |
| Si | 17.40 | 25.57 |
| Al | 4.14 | 5.84 |
| S | 1.17 | 2.11 |
| Ca | 2.78 | 4.79 |
| K | 0.55 | 1.12 |

| 300 °C | | |
|---|---|---|
| Element | At % | Wt % |
| O | 72.27 | 59.80 |
| Si | 16.79 | 25.58 |
| Al | 3.62 | 5.01 |
| Ca | 2.01 | 1.97 |

| 400 °C | | |
|---|---|---|
| Element | At % | Wt % |
| O | 71.00 | 61.63 |
| Si | 11.62 | 16.74 |
| Al | 3.48 | 5.09 |
| S | 4.12 | 7.77 |
| Ca | 1.01 | 1.97 |
| Na | 1.59 | 1.88 |

**Figure 2.** EDX spectra of clinoptilolite in various temperature treatments:
(a) 120 °C; (b) 300 °C; (c) 400 °C

For all selected temperatures, the content of elements in clinoptilolite treated at lower temperatures is higher than for clinoptilolite treated at higher temperatures. This difference in the metal release could be attributed to the partial breakdown of the clinoptilolite structure at high temperatures, together with the intense dehydration, which can lead to cell volume reduction and to exchangeable cations trapping in the zeolite channels (Bish et al., 2001).

The dominant elements were oxygen, silicon, and aluminum. The percentage of these elements are not constant and changes depend on the thermal modification. There are no significant differences in the percentage of oxygen, which varies from 73.96 to 71%. The slight decrease of aluminum and silicon in thermally modified samples of clinoptilolite at higher temperatures (300 and 400 $^{o}$C) is attributed to the removal of water molecules from the natural structure of clinoptilolite.

In addition to the mentioned elements, clinoptilolite also contains sodium, calcium, potassium, and sulfur, in smaller content which varies depending on the temperature.

The modification of clinoptilolite in various temperatures provides the similar Si/Al ratio. Si/Al ratio of clinoptilolite heated on 120 $^{o}$C is 4.2. After the increase of the temperature on 300 $^{o}$C, Si/Al ratio increases up to 4.64.

EDX analysis was carried out to examine the elemental distribution in the clinoptilolite framework after extraction procedure, and weight and atomic percentage of elements are presented in Table 2.

**Table 2.** Element compositions (at % and wt %) of the clinoptilolite thermally modified at 120 $^{o}$C, 300 $^{o}$C, and 400 $^{o}$C after spike with surrogates' standards and benzo[*a*]pyrene

| Element | 120 °C | | 300 °C | | 400 °C | |
|---|---|---|---|---|---|---|
| | (at %) | (wt %) | (at %) | (wt %) | (at %) | (wt %) |
| C | / | / | 47.82 | 19.49 | 43.87 | 21.26 |
| O | 65.99 | 48.49 | 12.10 | 6.57 | 33.44 | 21.59 |
| Si | 18.99 | 24.50 | 1.48 | 1.41 | 10.01 | 11.34 |
| Ba | | | | | 6.06 | 33.57 |
| Fe | 4.53 | 11.61 | 36.44 | 69.04 | 1.88 | 4.24 |
| Al | 4.40 | 5.45 | / | / | 1.73 | 1.89 |
| Co | / | / | 1.04 | 2.07 | / | / |
| S | 3.49 | 5.14 | 0.43 | 0.47 | / | / |
| K | 1.52 | 2.72 | 0.57 | 0.75 | 0.54 | 0.85 |
| Ca | 0.8 | 1.54 | / | / | 1.84 | 2.97 |
| Ti | 0.25 | 0.5 | 0.13 | 0.20 | / | / |

It can be seen that the ratio of elements has been changed. Major changes have occurred in the modification at 300 °C. The percentage of dominant elements has been changed drastically. The atomic percentage of oxygen, silicon and aluminum decreased from 72.27% to 12.10%, 16.74% to 1.48% and 3.62% to 0%, respectively. The EDX analysis revealed the highest percentage of carbon in the modification prepared at 300 °C. Carbon in this case originated from molecules of BaP. This fact indicates the suitability of this sorbent for bonding BaP. Also, a high atomic percentage of carbon can be observed in the modification achieved by preparing clinoptilolite modification at 400 °C, but the decrease in the percentage of dominant elements (oxygen, silicon and aluminum) is lower. Also, it could be expected that this modification will show great ability for sorption of BaP. Clinoptilolite prepared to 120 °C did not show significant changes in its composition after the treatment with the PAH surrogate standard.

## Extraction efficiency

The characterized clinoptilolite modifications (at 300 and 400 °C) were used to evaluate the extraction efficiency of BaP from spiked water samples.

PAH surrogate standards are chemically similar to target BaP and they behave in similar manner throughout the sample preparation and analysis procedures. 2,4,6-tribromophenol, 2-fluorobiphenyl and 2-chlorphenol-3,4,5,6-$d_4$ was used as a surrogate standard in order to monitor extraction efficiency (Ćirić et al., 2018). The acceptable range of surrogate recoveries was set to contain within 50 and 120% (Wnorowski et al., 2006). Results of recoveries are presented in Table 3.

**Table 3.** Recovery values of surrogate standards and benzo[*a*]pyrene for sorbent modifications - clinoptilolite thermally treated at 120 °C, 300 °C and 400 °C

| Modification | Spiking level (ppm) | 2, 4, 6-Tribromophenol | 2-Fluorobiphenyl | 2-Chlorphenol-3, 4, 5, 6-$d_4$ | Benzo[*a*]pyrene |
|---|---|---|---|---|---|
| Clinoptilolite modified at 120 °C | 0.5 | 78.04±0.59 | 72.75±0.26 | 57.07±0.46 | 85.5±0.72 |
| | 1.5 | 135.93±3.35 | 81.40±0.95 | 76.05±2.28 | 104.91±0.84 |
| Clinoptilolite modified at 300 °C | 0.5 | 98.60±3.19 | 90.68±0.76 | 82.44±3.25 | 117.75±1.16 |
| | 1.5 | 80.84±5.94 | 78.44±1.15 | 76.05±1.67 | 93.05±2.01 |
| Clinoptilolite modified at 400 °C | 0.5 | 86.03±0.15 | 87.88±0.25 | 81.84±0.82 | 117.26±3.24 |
| | 1.5 | 82.63±1.75 | 61.68±0.46 | 78.64±4.76 | 105.03±1.8 |

Obtained values for three mentioned standards were in recommended range. The best values were for clinoptilolite modified at 300 °C, for all three surrogate standards, 80.84–98.60% for 2, 4, 6- Tribromophenol; 78.44–90.68% for 2-Fluorobiphenyl and 76.05–82.44% for 2-Chlorphenol-3, 4, 5, 6$d_4$. Also, the modification at 400 °C showed similar results. It can be noticed that modifications at 300 °C and 400 °C show a higher value of recovery for model water samples with lower concentrations of BaP. BaP is the only polycyclic aromatic hydrocarbon with enough toxicological evidence (Moret et al., 2005) and that can be used when designing experiments for PAHs analysis. Recovery values of BaP using clinoptilolite termally modified at

300 $^{o}$C and 400 $^{o}$C are higher for 0.5 ppm spiking level than for 1.5 ppm. In contrast, modification at 120 $^{o}$C showed better recovery values for higher spiking level.

## Conclusion

The use and application of mesoporous materials to encapsulate pollutant particles has attracted a particular interest. For this reason, clinoptilolite was the subject of this study. Elemental and morphological features of thermally modified clinoptilolite at 120 $^{o}$C, 300 $^{o}$C and 400 $^{o}$C were performed using SEM-EDX. Mentioned sorbents were tested in a dispersive micro - solid phase extraction of BaP from water, using GC-MS.

SEM images indicate that there are no essential changes in the particles after thermal modification. EDX spectra show that the elemental composition of analyzed samples of clinoptilolite before and after extraction procedure is different. Before the extraction procedure, the content of elements is lower in thermally modified samples of clinoptilolite at higher temperatures (300 $^{o}$C and 400 $^{o}$C) than for clinoptilolite treated at 120 $^{o}$C. After the extraction procedure EDX analysis showed the highest percentage of carbon in the modification prepared at 300 $^{o}$C which indicates that the structure of the sorbent thus obtained is the most suitable for use in BaP studies. Based on recovery values for extraction efficiency, it can be concluded that modifications at 300 $^{o}$C and 400 $^{o}$C are more favorable for the analysis of BaP present in a lower concentration in the analyzed sample. However, the clinoptilolite sample that was thermally modified at 120 $^{o}$C showed better recovery values for a higher spiking concentration of BaP, so it can be concluded that its usage would be favorable for samples with higher BaP concentrations.

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## Conflict-of-Interest Statement

No potential conflict of interest was reported by the authors.

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