

## Removal of BTEX and hexane by organo-zeolites: The influence of surfactant carbon chain length on the sorption process

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### ABSTRACT

The synthetic zeolite Na-P1 and natural clinoptilolite are modified using dodecyl trimethyl ammonium bromide (DDTMA), didodecyl dimethyl ammonium bromide (DDDDMA), tetradecyl trimethyl ammonium bromide (TDTMA), ditetradecyl dimethyl ammonium bromide (DTDDMA), hexadecyl trimethyl ammonium bromide (HDTMA), dihexadecyl dimethyl ammonium bromide (DHDDMA), octadecyl trimethyl ammonium bromide (ODTMA) and dioctadecyl dimethyl ammonium bromide (DODDMA) in amounts of 1.0 of the external cation exchange capacity of the zeolites. The sorption performance of the zeolites and organo-zeolites for aqueous benzene, ethylbenzene, toluene, p-xylene (BTEX) and hexane are evaluated. After modification, the organo-zeolites show good performance for the removal of BTEX and hexane from the aqueous solution. The results show that the modification of the zeolites by surfactants with double-carbon chains (DDDDMA, DTDDMA, DHDDMA and DODDMA) improves the sorption properties for benzene, ethylbenzene and toluene. In the case of ethylbenzene, the sorption results are twice as high for the modified zeolites compared to the unmodified zeolites. Based on the experimental data, the removal efficiencies follow the order of hexane > ethylbenzene > toluene > p-xylene > benzene. Hexane was adsorbed in the greatest quantity on the zeolite (~75–80%) and all organo-zeolites (~90–95%). Benzene was adsorbed in the lowest quantity on the zeolite (40–50%) and the organo-zeolites (30–40%). Simultaneously, it is shown that the sorption efficiency increases with increasing carbon chain length. The sorption efficiency depends on the chemical properties of the various organic compounds and the duration of the sorption process.

**Keywords:** Adsorption; Zeolite Na-P1; Clinoptilolite; BTEX removal; Hexane removal; Surfactants

### 1. Introduction

Two of the major contaminants in groundwater systems are volatile organic compounds (VOCs) and hexane. These contaminants take decades to degrade and pose a significant threat to public health and the local environment [1].

Benzene, toluene, ethylbenzene and xylene (BTEX) are amongst the most well-known VOCs (Fig. 1). These aromatic hydrocarbons have detrimental effects on human health. BTEX are natural compounds found in crude oil, coal and gas deposits. Therefore, they are naturally present at low concentrations in groundwater abstracted from aquifers in the vicinity of such deposits [2–4]. The main source of BTEX contamination is through the leakage of underground gasoline storage tanks. They are also released from

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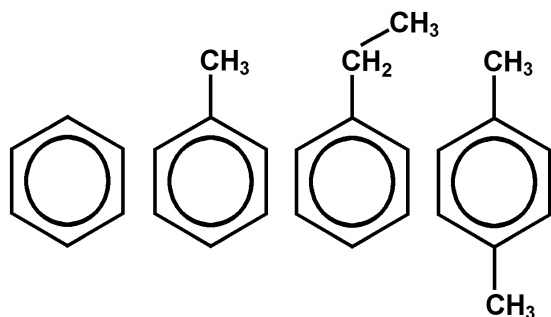


Fig. 1. Structural formulas of selected VOCs. From the left: Benzene, toluene, ethylbenzene and p-xylene.

large bulk facilities, surface spills and pipeline leaks. Hexane is a highly volatile component of the paraffin fraction of crude oil and natural gas, and it is a constituent of heating and motor fuels refined from petroleum. Hexane can be released to water from a number of sources, including industrial discharges, effluents from municipal waste-treatment plants and non point source runoff from roads and other surfaces [5]. In soil and water, the dominant transport mechanism for hexane is volatilization, but no experimental data focusing directly on hexane is available.

Several treatment methods have been developed to remove BTEX and hexane from industrial wastewater. They include ion exchange, filtration, adsorption and the use of various types of sorbents [6–9]. Recently, the need for an alternative low-cost, easily available mineral sorbent has driven the search for new materials. Zeolites, due to their unusual properties, such as a high specific surface area, stability, ion exchange, adsorption and molecular sieving, have been recognized as excellent sorbents [10,11]. Due to their negative charge, zeolites are excellent adsorbents of cationic metal ions [12–15]. Alternatively, the presence of a negatively-charged surface results in zeolites having little or no affinity for anions or polar organic compounds.

The possibility of changing the surface charge of zeolites and their application as sorbents of organic compounds has been described in the literature [16–19]. The replacement of exchangeable K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> ions by organic cations neutralizes the negative charge of the surface [20]. Surfactant introduction alters the chemistry of the zeolite surface, allowing zeolites to adsorb nonpolar organic solutes and inorganic anions [10,21].

On this basis, we carried out an investigation with the aim of preparing a series of organo-zeolites by the sorption of quaternary ammonium salts on the synthetic zeolite Na-P1 and clinoptilolite. The objective was to test the potential adsorption capacity for BTEX and hexane. The prospective sorbent should be relatively cheap and easy to prepare. Based on previous research, tests were performed on the organo-zeolites modified with a monolayer of surfactant (1.0 of external cation exchange capacity (ECEC)) [22].

## 2. Experimental

### 2.1. Materials

Synthetic zeolite Na-P1 and clinoptilolite from the Sokyrnytsya deposit (Trans Carpathian region, Ukraine)

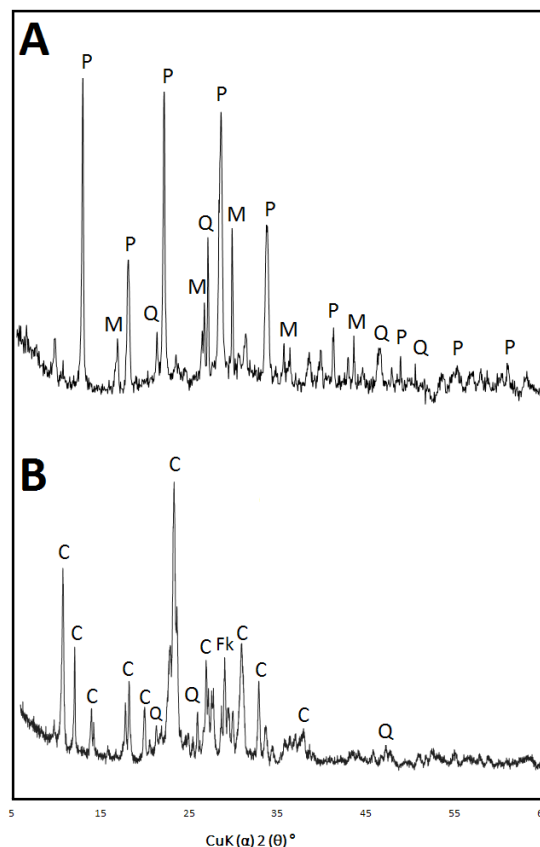


Fig. 2. X-ray diffraction patterns of: (a) – synthetic zeolite Na-P1; (b) – natural zeolite clinoptilolite.

were used in this study. This synthetic zeolite was produced from F-class fly ash (containing < 20% lime, CaO) supplied from the Rybnik power plant in Poland. The hydrothermal synthesis of Na-P1 was performed by mixing 20 g of fly ash with 400 ml of 3 M NaOH at 75°C for 24 h [23–25]. The resulting product was high-purity Na-P1 containing 81 wt.% of the Na-P1 phase with admixtures of mullite and quartz [25] (Fig. 2a). The natural zeolite used in the study was rich in clinoptilolite (~75%). Quartz and K-feldspar were identified as suitable admixtures [21] (Fig. 2b). Na-P1 has been described in previous studies [21,22,25], as has clinoptilolite from the Sokyrnytsya deposit [21,26,27]. The ECEC was determined through the indication of the maximum amount of quaternary ammonium salts attached to the zeolite surface [22] and was 24.4 meq/100 g for Na-P1 and 11.45 meq/100 g for clinoptilolite.

### 2.2. Modification

Since the ammonium salt molecules are too large to enter the zeolite channels, the modification of the zeolites takes place only on the outer surface of the crystallites [28]. Therefore, the ECEC is important in the synthesis of organo-zeolites. Na-P1 and clinoptilolite were modified by:

- Dodecyl trimethyl ammonium bromide (DDTMA);
- didodecyl dimethyl ammonium bromide (DDDDMA);

- tetradecyl trimethyl ammonium bromide (TDTMA);
- ditetradecyl dimethyl ammonium bromide (DTDDMA);
- hexadecyl trimethyl ammonium bromide (HDTMA);
- diheksadecyl dimethyl ammonium bromide (DHDDMA);
- octadecyl trimethyl ammonium bromide (ODTMA);
- dioctadecyl dimethyl ammonium bromide (DODDMA),

in amounts of 1.0 of the ECEC of the zeolites (Table 1). Previous research proved that a modification of 1.0 of the ECEC is the best sorbent of BTEX [22]. In order to obtain a surfactant coverage of 1.0 ECEC, it was necessary to use 24.4 and 11.45 mM of surfactant per 100 g of Na-P1 and clinoptilolite, respectively. Each of the organo-zeolites were prepared by mixing 50 g of zeolite with 1000 g of the surfactant solutions at a concentration of 1.0 of the ECEC. After 8 h of stirring at 60°C, the samples were centrifuged and dried at 60°C. This procedure is well documented [22] and has proved to be highly effective. Calculations of the modification efficiency were made by comparing the content of carbon, hydrogen and nitrogen in the samples before and after modification. The coverage of the surfactant was estimated by comparing the amount of surfactants adsorbed on the zeolite surfaces with the ECEC (Table 1).

### 2.3. Sorption of BTEX and hexane

All chemicals used in this study (benzene, toluene, ethylbenzene, p-xylene, hexane and methanol) were of analytical grade and purchased from Sigma-Aldrich. The solubilities of BTEX and hexane in water at 20°C are 0.188, 0.067, 0.015, 0.20 and 0.014%, respectively [29]. To improve their solubility, the adsorption of BTEX and hexane was made in a mixture of distilled water and methanol. Stock concentrations were designed to maintain a methanol concentration of 0.2 vol.% in the initial aqueous solutions. This amount of methanol has no measurable effect on the sorption [30]. The concentrations of working water solutions were 50 ppm. All presented results are based on the average of two measurements.

Experiments on the influence of time on the sorption of VOCs onto zeolites allowed for the practical determination

of the time necessary for the effective immobilization of the compounds. For kinetic studies, an initial concentration of  $C_0 = 50$  ppm was selected and the suspension samples were collected after 1, 2, 15, 30, 60, 120, 240, 360, 720 and 1440 min of the reaction.

To conduct experiments of BTEX and hexane removal from aqueous solutions by various modifications of Na-P1 and clinoptilolite, the samples were placed in a 7 ml centrifuge polypropylene tube and 5 ml of a solution containing each hydrocarbon was added. The mixtures were shaken for 2 h and centrifuged at 14000 rpm for 10 min until the washing solution was cleared and then decanted. Analysis of the influence of time on the efficiency of sorption showed that 2 h was the optimal time that can be accepted for subsequent experimental analysis. The time of shaking was shortened compared to the previous experiments [22] because of the high volatility of the analyzed hydrocarbons and the possible loss of these compounds during one day of shaking. The BTEX concentration was subsequently determined using GC/MS. Each solution was diluted ten times before a chromatographic analysis was undertaken. By comparing the initial concentration with the equilibrium concentrations, the sorption efficiency could be determined.

### 2.4. Analytical methods

Solids were analyzed by X-ray diffraction (XRD) with an X-ray powder diffractometer (Philips APD PW 3020 X'Pertdiffractometer with a graphite monochromator) using Cu-K $\alpha$  radiation, a step size of 0.05° 2 $\theta$  and a scan rate of 1 s per step. The chemical compositions of the investigated zeolites were determined using sequential wavelength dispersive X-ray fluorescence (WDXRF) spectroscopy with a RIGAKU ZSX Primus II with a Rh anode (4.0 kW). The samples were ground to a particle size of 200-mesh and then calcined at 1000°C. The calcined samples were then homogenized with flux (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) in a ratio of 1:10 and melted at 1050°C until glass pastilles with a diameter of 25 mm were obtained. The system allowed for a multi-element detection of elements from boron to uranium. The ECEC and efficiency of the modification of the organo-zeolites were calculated on the basis of the contents of carbon, hydrogen and nitrogen in the samples using an ElementarVarioEL III CHNS automatic analyzer. The specific surface area and porosity were determined from N<sub>2</sub> gas adsorption/desorption isotherms at 77 K after outgassing for 12 h at 373 K using ASAP 2020 apparatus (Micromeritics). The BET equation was used for specific surface area calculations ( $S_{\text{BET}}$ ) [31]. The total pore volume ( $V_{\text{tot}}^{0.99}$ ) was calculated from the amount of N<sub>2</sub> adsorbed at a relative vapor pressure ( $P/P_0$ ) of ~0.99.

The BTEX and hexane concentrations were determined using a Hewlett Packard GC/MS system (HP 6890/5973) coupled with a headspace sampler (HP 7694E). For the analysis of hydrocarbons, 10 mL of analytical solution was placed in 20-mL vials and sealed hermetically with silicone septum caps. These vials were introduced into the oven of the headspace sampler, in sequence, at a temperature of 70°C for 30 min. Then, the volatiles filled the loop (120°C) and were injected into the chromatographic system through a thermostatted transfer line heated to 160°C. An HP-5MS capillary column was used for the chromatographic separations (30 m  $\times$  0.25 mm; film thickness of 0.25  $\mu$ m, meth-

Table 1  
Efficiency of zeolite Na-P1 (Na-P1) and clinoptilolite (Cp) modification to the organo-zeolites by adsorption of an organic surfactants

	Na-P1		Cp	
	Adsorption [mM/100 g]	Multiples of ECEC	Adsorption [mM/100 g]	Multiples of ECEC
DDTMA	21.06	0.94	10.53	0.71
TDTMA	23.18	0.98	10.31	0.71
HDTMA	23.91	1.06	10.76	1.04
ODTMA	23.67	1.04	10.65	0.93
DDDDMA	21.72	0.89	9.73	0.84
DTDDMA	21.96	0.90	10.01	0.88
DHDDMA	22.45	0.92	10.31	0.90
DODDMA	22.45	0.92	10.19	0.89

yl-(5%)-phenylsiloxane phase), purchased from J&W Scientific. The column was initially maintained at 55°C for 3 min, then the temperature was increased to 120°C at a rate of 15°C/min, which was then held for an additional 1 min. Helium was used as the carrier gas at a flow rate of 1 mL/min. Data collection was performed using Enhanced ChemStation ver.A.03.00 software. MS was carried out in SCAN mode with  $m/z$  range of 24–160 amu, an ionization voltage of 70 eV and the temperature of the ion source and quadrupole were 230 and 150°C, respectively.

### 3. Results and discussion

#### 3.1. Materials characterization

Analysis of the elemental composition revealed that Na-P1 is a low Si-phase rich in sodium cations (Table 2), with a Si/Al ratio of 2:1. This ratio is characteristic for a synthetic faujasite-type zeolite Y. High calcium and iron contents are characteristic of synthetic zeolites, resulting from the chemical composition of fly ash (Table 1). The presence of residual carbon after the coal combustion process is also typical (C = 3.8 wt.% from the analysis of CHNS). Na-P1 had type II isotherms with a hysteresis loop of type H2 (Fig. 2). It also has a BET specific surface area of 74.91 m<sup>2</sup>/g, with a total pore volume of 0.225 cm<sup>3</sup>/g (Table 3). Textural studies have shown the lowest proportion of micropores ( $V_{mic} = 0.030$  cm<sup>3</sup>/g) in relation to the volume of all pores (13%).

Table 2  
XRF analysis (wt%) of the major elements of synthetic zeolite Na-P1 and clinoptilolite

	Na-P1	Cp
Na <sub>2</sub> O	4.80	0.68
MgO	1.58	0.92
Al <sub>2</sub> O <sub>3</sub>	18.00	12.10
SiO <sub>2</sub>	42.10	71.30
K <sub>2</sub> O	0.87	3.34
CaO	14.70	3.07
TiO <sub>2</sub>	0.84	0.18
MnO		0.06
Fe <sub>2</sub> O <sub>3</sub>	5.92	1.89
LOI	11.2	6.40

Table 3  
Porous texture parameters. Cp – clinoptilolite, Na-P1 – zeolite Na-P1. Abbreviations of surfactants: 12 – DDTMA, 14 – TDTMA, 16 – HDTMA, 18 – ODTMA

	Cp	Cp 12	Cp 14	Cp 16	Cp 18
$S_{BET}$ [m <sup>2</sup> /g]	15.88	6.96	5.30	4.97	4.71
$V_{tot}^{0.99}$ [cm <sup>3</sup> /g]	0.047	0.037	0.034	0.032	0.031
	Na-P1	Na-P1 12	Na-P1 14	Na-P1 16	Na-P1 18
$S_{BET}$ [m <sup>2</sup> /g]	74.91	59.51	41.25	36.68	20.40
$V_{tot}^{0.99}$ [cm <sup>3</sup> /g]	0.225	0.256	0.219	0.218	0.184

The proportion of macropores was 15% ( $V_{mac} = 0.034$  cm<sup>3</sup>/g). Mesopores occupied the greatest volume,  $V_{tot} = 72%$  ( $V_{mes} = 0.161$  cm<sup>3</sup>/g) (Table 3).

The Si/Al ratio for clinoptilolite is 5:2. This ratio indicates a stronger stability in aqueous environments because of an increase in the hydrophobic character of the zeolite. The high Si and K contents confirmed that the natural zeolite is clinoptilolite-Ca. Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> were identified as the exchangeable cations, with Ca<sup>+</sup> being predominant (Table 2) [21,26,27]. The natural zeolite had a type II isotherm with a hysteresis loop of type H3 (Fig. 3). This indicates a mesoporous character with the formation of slit-shaped pores, which arise from the stacking of crystal particles [32,33]. The specific surface area of natural clinoptilolite is 15.88 m<sup>2</sup>/g and the total pore volume is 0.047 cm<sup>3</sup>/g. Mesopores ( $V_{mes} = 0.027$  cm<sup>3</sup>/g) have the largest share of the total pore volume (57%). The low share of micropores (13%) relative to the total pore volume is characteristic of clinoptilolite (Table 3).

Both tested zeolites contain significant oxide concentrations, but they are mainly composed of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The proportions between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are connected to the Si/Al ratio, on the basis of which the surface charge and surface properties can be determined. The synthetic zeolite exhibits better porosity, however, it has a lower Si/Al ratio. These properties cause the increased hydrophilic nature of Na-P1 and make it less stable in aqueous solutions [34].

#### 3.2. Organo-zeolites

The modification efficiency represents the amount of surfactant attached to the surface of the zeolite. When the amount of adsorbed surfactant is equal to the ECEC of the zeolite, the modification efficiency is 100%. Table 1 shows the effectiveness of the zeolite modification in the given conditions. The results of the CHN analysis were compared with the results of the FTIR analysis, which confirmed the

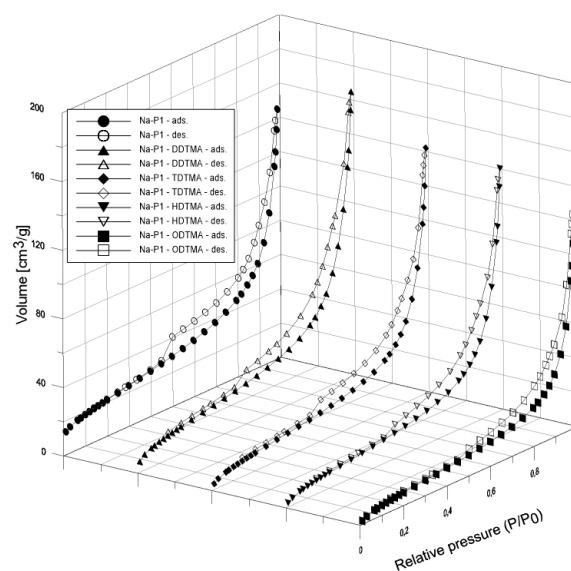


Fig. 3. Comparison of N<sub>2</sub> adsorption and desorption isotherms at -196°C for Na-P1 and its single modifications.



effectiveness of the modification [35]. In most cases, a modification efficiency of more than 90% was observed. The modification efficiency increases with increasing carbon chain length of the surfactant. The synthetic zeolite Na-P1 is easier to modify as it is less contaminated than the natural zeolite. Only when using the DDTMA and TDTMA surfactants during the surface modification of clinoptilolite did the resulting organo-zeolites have a lower modification efficiency. Surface modification reduces the total pore volume ( $V_{tot}^{0.99}$ ) and specific surface area ( $S_{BET}$ ) of zeolites (Table 3). For example, Na-P1 modified by TDTMA, HDTMA and ODTMA in an amount of 1.0 ECEC had specific surface area of 41.3, 36.7 and 30.4 m<sup>2</sup>/g, respectively. The reduction of  $S_{BET}$  is more than 50% compared to the unmodified material (74.91 m<sup>2</sup>/g) (Table 3). Na-P1 modified with DDTMA, TDTMA, HDTMA and ODTMA had a composite of type II and type IV isotherms with a hysteresis loop of type H2, similar to the Na-P1 zeolite before modification (Fig. 3). A similar relationship was observed for the TDTMA-, HDTMA- and ODTMA-modified clinoptilolite, where the  $S_{BET}$  values were 5.30, 4.79 and 4.71 m<sup>2</sup>/g, respectively. Compared to the starting material (15.88 m<sup>2</sup>/g),  $S_{BET}$  was reduced by more than 70% (Table 3). The specific surface area for Na-P1 and its modifications is much higher than for clinoptilolite and organo-clinoptilolites. Similar relationships were determined for the total pore volume ( $V_{tot}^{0.99}$ ). Surfactants attached to the zeolite surfaces may block the porosity. The longer the surfactant molecule, the more limited the porosity (Table 3). In the case of BTEX and hexane sorption on organo-zeolites, the hydrocarbons are dissolved in the organic layer of the surfactant. The organo-clinoptilolite modified by surfactants shows a similar type of isotherm and hysteresis loop (type H3) as natural clinoptilolite (Fig. 4).

### 3.3. Influence of time on VOC sorption

The exemplary kinetic curve for the sorption of benzene is presented in Fig. 5. The influence of time on the sorption

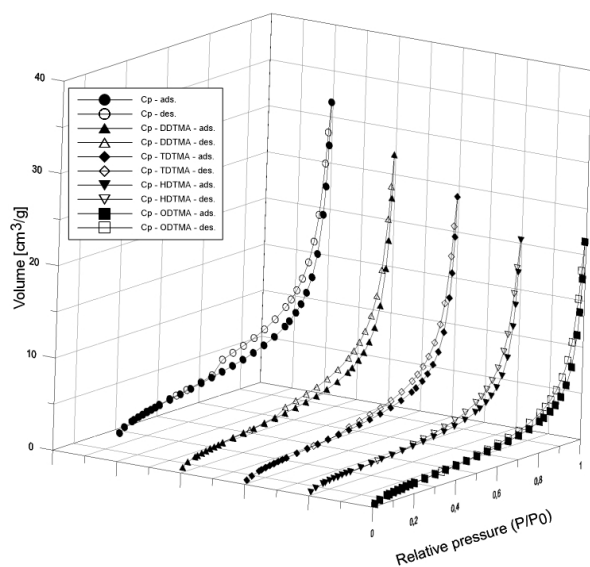


Fig. 4. Comparison of N<sub>2</sub> adsorption and desorption isotherms at -196°C for clinoptilolite and its single modifications.

was shown to be similar for all the organic compounds and surfactants tested. It is important to determine the shortest time in which the sorption efficiency is satisfactory, as many studies have shown a high evaporation of VOCs from aqueous solutions [36,37]. The greatest differences in the sorption efficiency were observed within the first 2 h of the reaction. After 1 min of contact with the sorbent solution, 95% of the initial concentration of benzene remained in the solution. Within 1 h, only half of the initial concentration of benzene remained in the solution (54%). A significant decrease in the concentration of benzene between 1 (54%) and 2 h (45%) of the reaction was observed. The changes in concentration were not significant and could be related to the evaporation of volatile compounds from the solution. Therefore, 2 h was sufficient for the complete sorption of benzene. Although equilibrium was not achieved, we did not want to risk measurement irregularities from the evaporation of organic compounds from aqueous solutions. Identical dependencies were registered for toluene, ethylbenzene, xylene and hexane.

### 3.4. Removal of BTEX and hexane

Based on the experimental data, the removal efficiencies for a single-solute system depend on the organo-zeolite used and follow the order of (Table 4) ethylbenzene > toluene > p-xylene > benzene for sorption on organo-zeolites based on Na-P1 and toluene > p-xylene > ethylbenzene > benzene for sorption on organo-clinoptilolites. The removal efficiencies for the unmodified zeolites follow the order of xylene > toluene > ethylbenzene > benzene (Table 4). The BTEX removal efficiency depends not only on the type of zeolite or surfactant used for modification, but also on the chemical properties of the various organic compounds, such as dipole moment, mass molar, molecule structure, functional groups (Table 5), the time of the sorption process and the hydrophobicity of each analyte, and other physico-chemical and thermochemical properties (Table 5) [38].

The removal efficiency of benzene from the aqueous solution is presented in Fig. 6. A benzene molecule is composed of six carbon atoms joined in a ring, with one hydrogen atom attached to each carbon atom (Fig. 1). The zero

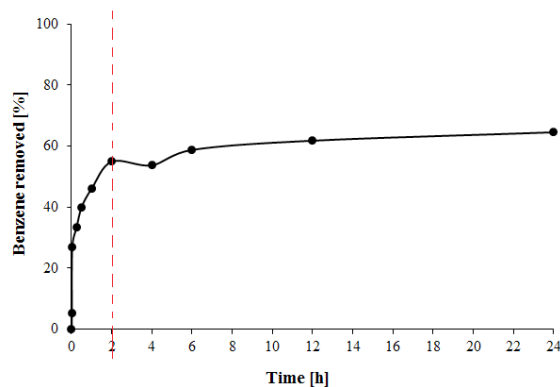


Fig. 5. Influence of reaction time on sorption efficiency. For example, Na-P1 modified with HDTMA in an amount of 1.0 ECEC, with a starting benzene concentration of 50 ppm.

Table 4

Amount of adsorbed BTEX and hexane on zeolites and organo-zeolites (mg/g). Initial concentration of hydrocarbons 50 ppm

Sample	Benzene	Toluene	Ethylbenzene	p-Xylene	Hexane
Na-P1	0.21	0.84	0.81	1.47	1.99
*DDTMA	0.68	1.58	1.19	1.55	2.20
*TDTMA	0.94	1.72	2.13	1.61	2.01
*HDTMA	1.24	1.74	2.14	1.64	2.20
*ODTMA	1.31	1.70	2.20	1.65	2.04
*DDDDMA	1.06	1.57	2.20	1.65	2.10
*DTDDMA	1.37	1.95	2.35	1.67	2.16
*DHDDMA	1.36	2.07	2.14	1.63	2.17
*DODDMA	1.17	2.17	1.94	1.63	2.05
Clinoptilolite	0.62	1.66	0.30	0.99	2.18
*DDTMA	0.66	1.88	0.55	1.15	2.23
*TDTMA	1.09	1.85	0.60	1.24	2.43
*HDTMA	1.18	1.87	0.67	1.22	2.45
*ODTMA	1.20	1.95	0.66	1.26	2.46
*DDDDMA	1.24	1.96	1.21	1.50	2.46
*DTDDMA	1.42	1.97	1.50	1.51	2.45
*DHDDMA	1.45	1.98	1.61	1.38	2.46
*DODDMA	1.72	1.94	1.52	1.37	2.45

Table 5

Physicochemical and thermochemical parameters of BTEX and hexane [39]. M – molar mass;  $S_w$  – solubility in water (20°C);  $B_p$  – boiling point;  $H_c^\circ$  – standard molar enthalpy change of combustion at 298 K;  $H_f^\circ$  – standard molar enthalpy change of formation at 298 K;  $G_f^\circ$  – standard molar Gibbs free energy change of formation at 298 K;  $S^\circ$  – standard molar entropy at 298 K (standard pressure 1 atm).

	Benzene	Toluene	Ethylbenzene	Paraxylene	Hexane
M, g/mol	78.11	92.14	106.17	106.16	86.18
$S_w$ , %	0.188	0.067	0.015	0.024	0.014
Dipole moment [D]	0	0.036	0.58	0.07	0.08
$B_p$ , °C	80	111	136	138	69
$H_c^\circ$ , kJ/mol	–3267	–3910	–4564	–4553	–4163
$H_f^\circ$ , kJ/mol	49.0	12.1	–13.1	–24.4	–198.6
$G_f^\circ$ , kJ/mol	124.5	110.6	19.7	110.3	–4.2
$S^\circ$ , J/mol·K	172.8	319.7	255.2	247.2	295.9

dipole moment indicates the apolar nature of benzene (Table 5). Sorption experiments were conducted under a concentration of hydrocarbon of 50 ppm. Clinoptilolite was more effective in the removal of benzene, both before and after modification, than zeolite Na-P1 and its modifications (Fig. 6). The explanation for this might be more due to the hydrophobic nature of the clinoptilolite, resulting from the Si/Al ratio. The surface modification of zeolites significantly improves the modification efficiency. Before the modification process, Na-P1 and clinoptilolite removed 7 and 22% of benzene from the solution, respectively (Fig. 6). After modification, the synthetic zeolite removed up to 50% of benzene, with DHDDMA-modified Na-P1 being the most effective sorbent. However, DODDTMA-clinoptilolite removes over 60% of benzene. The sorption efficiency increases with increasing carbon chain length. The use of surfactants with

two carbon chains further improves the process of removing benzene from the solution. The reason for this is the creation of a more extensive organic layer that dissolves organic compounds. Compared to other hydrocarbons, benzene had the poorest sorption efficiency (Table 4) as a result of its increased hydrophobic character compared to other VOCs.

For toluene removal from the aqueous solution ( $C_0 = 50$  ppm), clinoptilolite and its modifications were identified as better sorbents than Na-P1 and its modifications in most cases (Fig. 7). Only Na-P1 modified by DHDDMA and DODDMA proved to be better sorbents compared to organo-clinoptilolites, and removed 70% and 75% of toluene, respectively. The surface modification significantly improves the sorption efficiency of the synthetic zeolite. Na-P1 removes only 30% of toluene, whereas its modification with DODDTMA removes over 75% of the initial con-

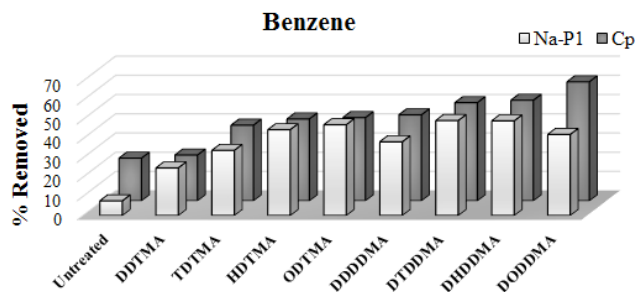


Fig. 6. Efficiency of benzene removal from aqueous solutions ( $C_0 = 50$  ppm,  $t = 2$  h).

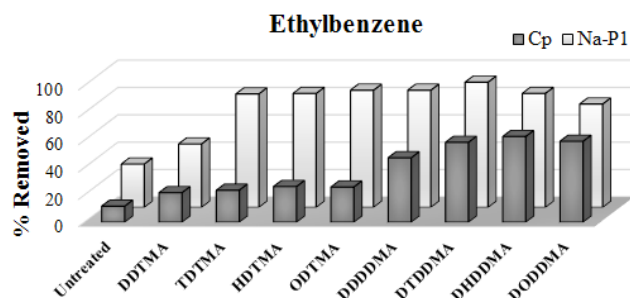


Fig. 8. Efficiency of ethylbenzene removal from aqueous solutions ( $C_0 = 50$  ppm,  $t = 2$  h).

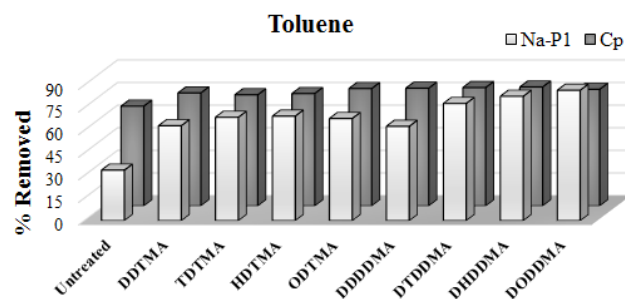


Fig. 7. Efficiency of toluene removal from aqueous solutions ( $C_0 = 50$  ppm,  $t = 2$  h).

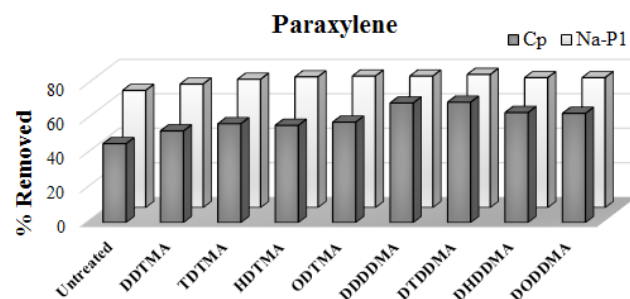


Fig. 9. Efficiency of p-xylene removal from aqueous solutions ( $C_0 = 50$  ppm,  $t = 2$  h).

centration. The surface modification of clinoptilolite did not have as high an influence on the sorption process as in the case of Na-P1. The sorption efficiency of the organo-clinoptilolite was only 8–13% higher compared to the unmodified sample. A 1 g sample of organo-zeolite removed 2.2 mg of toluene in the chosen process conditions ( $t = 2$  h,  $C_0 = 50$  ppm) (Fig. 7). The type of surfactant used in the modification did not have a major influence.

In the case of ethylbenzene sorption, the situation is reversed as the synthetic zeolite and its modifications are better sorbents than clinoptilolite and organo-clinoptilolites (Fig. 8). The surface modification had a greater influence on the improvement of the sorption properties of Na-P1. The minimum amount of removed ethylbenzene was recorded for the unmodified sample as 30%. After the modification of Na-P1 with DTDDMA, the maximum amount of ethylbenzene removed was 91%. The modification of the synthetic zeolite with surfactants with a carbon chain above 14C (HDTMA and ODTMA), as well as the use of surfactants with a double-carbon chain (DTDDMA, DHDDMA and DODDDMA), increases the sorption capacity in terms of ethylbenzene by over 1.5 mg/g (Table 4). At this stage in the process, clinoptilolite removed 11% of ethylbenzene from the solution. The best modification, DHDDMA-clinoptilolite, removed 53% of the toluene. The use of surfactants with a double-carbon chain in the modification of clinoptilolite clearly improves the sorption efficiency of toluene.

Similar phenomena are observed for the sorption of p-xylene (Fig. 9). Na-P1 is significantly more efficient in the removal of p-xylene than clinoptilolite. However, the modification process had little effect on improving the sorption

efficiency. Surface modifications improved the efficiency by ~8 and 20% for zeolite Na-P1 and clinoptilolite, respectively. Moreover, there is no clear relationship between the surfactant used and an improvement in the sorption properties of zeolites. The zeolites removed 1.0–1.7 mg of p-xylene per 1 g of zeolite (Table 4).

These studies have shown that Na-P1 and its organic modifications are better sorbents for ethylbenzene and p-xylene, while clinoptilolite and organo-clinoptilolites more efficiently remove benzene and toluene. Volatile compounds with a higher molecular weight (Table 5) are more freely adsorbed by the synthetic zeolite. There was also a correlation between the aqueous solubility of BTEX and the sorption process. More soluble compounds (Table 5) were more easily adsorbed by Na-P1. Also, the higher the dipole moment and boiling point, the better the sorption on the synthetic zeolite. Attention should also be paid to the thermodynamic parameters (Table 5), as the higher the values of these parameters, the better the clinoptilolite sorbent is.

Hexane is one of the first compounds removed from the solutions. Zeolite surface modification does not affect it; or is of little importance on the efficiency of sorption of hexane (Fig. 10). In all cases, more than 80% of hexane was removed from the solution. Clinoptilolite and its modifications were better sorbents and removed 2.2–2.5 mg of hexane per 1 g of material. Organo-clinoptilolites always removed 10–15% more hexane than organo-zeolites Na-P1. The physicochemical and thermochemical properties of hexane are similar to BTEX. The high level of hexane removed may be related to the structure of the molecule. In contrast to BTEX, which are aromatic compounds with a ring structure, hexane is an

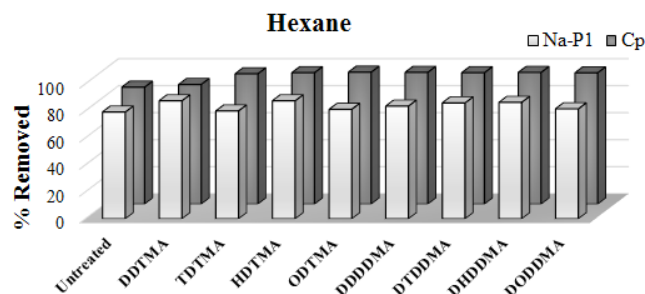


Fig. 10. Efficiency of hexane removal from aqueous solutions ( $C_0 = 50$  ppm,  $t = 2$  h).

alkane of six carbon atoms and the structure of a straight carbon chain. Its small particle size allows better access to the zeolite surface and its pores.

#### 4. Conclusions

The surface modification of zeolites improves their sorption ability in relation to VOCs. Hexane was removed efficiently by both zeolites and organo-zeolites. The conducted experiments showed that a duration of ~2 h is sufficient to carry out the reaction. The more hydrophobic the compound, the smaller the amount removed from the solution. Textural properties do not affect the sorption efficiency. The reaction only takes place on the outer surface of the material. The surface modification results in a significant reduction of all textural parameters.

The type of surfactant strongly affects the sorption efficiency. It is associated with the sorption mechanism of organic compounds on organically-modified minerals. The organic compounds are dissolved in the organic layer of the surfactant on the surface of the zeolite. Therefore, the more surfactant attached to the surface of the zeolite, the greater the efficiency in the removal of organic compounds. Subsequently, the longer the carbon chain in the surfactant, the greater the organic layer and the higher the sorption. Improving the sorption properties during the use of surfactants with two carbon chains forms an even larger organic layer, where BTEX and hexane dissolve. The properties of zeolites, in particular the Si/Al ratio, determine their sorption capacity. The higher the Si/Al ratio, the better the sorbents of organic compounds the zeolites are. The hydrophobicity of the zeolites is a more important element than their textural parameters in the case of the sorption of organic compounds. The sorption efficiency is also dependent on the physicochemical properties of the organic compounds and their thermodynamic parameters.

#### Acronyms

VOCs	— Volatile organic compounds
BTEX	— Benzene, toluene, ethylbenzene, and p-xylene
ECEC	— External cation exchange capacity
DDTMA	— Dodecyl trimethyl ammonium bromide
DDDDMA	— Didodecyl dimethyl ammonium bromide

TDTMA	— Tetradecyl trimethyl ammonium bromide
DTDDMA	— Ditetradecyl dimethyl ammonium bromide
HDTMA	— Hexadecyl trimethyl ammonium bromide
DHDDMA	— Dihexadecyl dimethyl ammonium bromide
ODTMA	— Octadecyl trimethyl ammonium bromide
DODDMA	— Dioctadecyl dimethyl ammonium bromide
XRD	— X-ray diffraction
WDXRF	— Wavelength dispersive X-ray fluorescence

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