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# BTX sorption on Na-P1 organo-zeolite as a process controlled by the amount of adsorbed HDTMA

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## ABSTRACT

The main objective of the study was to utilize fly ash by transforming it into Na-P1 zeolite. The obtained synthetic zeolite has been modified with a HDTMA surfactant in amounts of: 0.2, 0.4, 0.6, 0.8 and 1.0 of external cation exchange capacity (ECEC). The process reported hereunder was designed at room temperature (20 °C) and a low solid/solution ratio (1:2). Infrared spectroscopy (FTIR) was used to determine the quantity of the adsorbed surfactant on the crystallites' surface. The normalized intensity of the selected bands was compared with CHN results. The results revealed a very strong correlation between spectroscopic and chemical analyses and enabled the preparation of calibration curves. The sorption properties of organo-zeolites towards benzene, toluene, p-xylene (BTX) were evaluated. The results showed that the modification of the Na-P1 zeolite by HDTMA improves the sorption properties in terms of benzene and toluene and that 1.0 ECEC modification proved to be the best sorbent of those compounds. Xylene was adsorbed in the greatest quantity, however, sorption efficiency from aqueous solutions does not depend on the amount of surfactant used. Experiments proved that it is possible to remove more than 95% of toluene and xylene and more than 85% of benzene contaminants from aqueous solutions.

## 1. Introduction

Zeolites are well-known microporous crystalline solids with neutral $SiO_2$ groups and negatively charged $(AlO_2)^-$ ions compensated by non-framework cations such as $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ or $NH_4^+$ [1]. Cation exchange properties of traditional aluminosilicate zeolites arise from the isomorphous positioning of aluminum in tetrahedral coordination within their Si/Al frameworks ($Si^{+4} \rightarrow Al^{3+}$) [2]. Zeolites possess a few basic properties such as: high surface area, stability, ion exchange, adsorption and molecular sieving [3,4]. Those properties are exploited in a wide range of applications, e.g. in catalysis [5–7], ion-exchange (wastewater treatment) [8–11] and in the separation and removal of gases [12] and solvents [13,14]. However, natural zeolites contain admixtures which reduce the purity of their composition. Moreover, natural zeolites' properties (CEC, charge, size of cavities etc.) make it difficult to use them in specific chemical processes – further perpetuating the demand for synthetic zeolites.

Most of the world's produced fly ashes are solid wastes of coal combustion in the generation of electricity. However, they are also very attractive for recycling [15]. In recent years, the possibility of using fly ash from the combustion of coal for the synthesis of zeolite materials has been examined [15–18]. The obtained results show that fly ash can be used for direct hydrothermal synthesis [19–21], hydrothermal synthesis from alkali-fused fly ash [22], and hydrothermal synthesis of zeolites using extracted silica [23] or mine waters [17]. Hydrothermal synthesis of fly ash with a solution of NaOH at 95 °C for 24 h brings a high purity zeolite and has been adapted to the industrial production of zeolites on a large scale [24]. The resultant zeolites possess both a high surface area and stability [16].

One of the many uses of zeolites is their application in removing harmful compounds from contaminated soils and waters [9,25,26]. Zeolites have been especially useful in removing cationic species such as ammonium [27,28] and heavy metals [29–32]. A significant number of studies have suggested that the area of application could be expanded by utilizing the zeolite's surface [3]. Most zeolites are hydrophilic, therefore they are frequently modified to increase their surface hydrophobicity to adsorb low soluble compounds. The hexadecyltrimethylammonium bromide (HDTMA) is a long-chain cationic surfactant that possess a permanent positive charge and is one of the more popular surfactants [9]. In contact with the zeolite, HDTMA organic cations selectively exchange with the inorganic cations ($K^+$, $Na^+$, $Ca^{2+}$ or $Mg^{2+}$) on the surface of the zeolite crystals and form a surfactant layer with anion exchange

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properties [9,33]. Since the size of organic molecules is bigger than the pore diameter of zeolite, surfactants are attached on the external surface, leaving the internal pore accessible for adsorbate molecules [34]. Therefore, external cation exchange capacity (ECEC) is an important property in the synthesis of organo-zeolites.

The surfactant layer on organo-zeolites is a solvent-like medium into which non-polar organic compounds tend to dissolve. It is now recognized that sorption of organic compounds on surfactant-modified zeolite (SMZ) is a feasible method for the removal of pollutants from wastewaters [35,36]. The use of zeolites to remove compounds such as phenol, acetone, trichloromethane, pentanol and cresol with different water solubilities onto SMZ are well described in the literature [35,37–39]. An important trend is to adapt the zeolites for removing volatile organic compounds such as BTEX (benzene, toluene, ethylbenzene, xylenes) [40–44]. The chemical and petrochemical industries are often the source of BTEX contaminants through the wastewater they generate. Rigorous regulations have been imposed in terms of acceptable concentrations of these compounds in water because of their toxicity to human health and for the environment [37,45]. So far, these compounds are removed through the use of methods such as thermal oxidation, catalytic oxidation, absorption, condensation, membrane separation and adsorption. It has been found that adsorption is one of the most efficient methods to remove organic pollutants in wastewaters [40–42].

Until now, in order to determine the effectiveness of modification, two methods were used: Analysis of HDTMA concentration in the solution before and after modification using chromatographic methods or comparing the content of carbon, hydrogen and nitrogen in the samples before and after modification [40–44]. The usefulness of the FTIR method to probe the structure, organization of surfactant molecules in the interlayer space of layered zeolites as well as the analysis of the influence of the carbon chain length on the appearance of the FTIR spectrum has been documented [38]. The fact that the intensity of the bands changes with the amount of surfactant attached has been previously recognized [38,45]. However, the adaptation of the FTIR method for rapid analysis of the effectiveness of modification has not been described before.

The objective of our research was to optimize the modification process so that it is suitable for use on an industrial scale. Another challenge was to eliminate the problem of determining the effectiveness of the modification, as well as to examine whether the amount of surfactant affects the sorption efficiency.

## 2. Experimental

### 2.1. Zeolite Na-P1

As a substrate for the synthesis reaction of the zeolite Na-P1, the F-class fly ash (contains less than 20% lime – CaO) from the combustion of coal at the Rybnik power plant in Poland has been used. The chemical composition of fly ash was as follows (in wt%): $SiO_2$ – 52.1, $Al_2O_3$ – 32.2, $Fe_2O_3$ – 5.2, MgO – 1.3, CaO – 1.2, $Na_2O$ – 0.5, $K_2O$ – 2.9. The 4.6 wt% was lost during calcination and through marginal components not relevant to the synthesis process [46,47]). In terms of mineralogy, quartz was the dominant phase, in addition, mullite, magnetite and hematite have been identified (Fig. 1A). Spherical forms of aluminosilicate glass dominated the mineralogical composition (Fig. 2A).

For the synthesis of Na-P1 zeolite, technology developed by Franus (2011) has been used [24]. The following reaction conditions have been applied: 20 kg of fly ash; 12 kg NaOH, 90 $dm^3$ of $H_2O$; temperature of the process at 80 °C and for a duration of 36 h [24,47]. The resulting product was a high purity (81 wt%) Na-P1 zeolite. In addition to the Na-P1 phase, the presence of mullite and quartz phases have been identified (Fig. 1B). To calculate the quantitative content of Na-P1 the Rietveld method with the use of the computer program ''FullProf'' has been applied. Average ratios of individual cations are as follows: (Na + K + Ca + Mg)/Si = 0.44; Si/Al = 1.42 [16,47]. Na-P1 zeolite has BET specific surface area of 88 $m^2/g$, which is almost 6 times higher with respect to fly ash (15 $m^2/g$) [47]. Sodium is the main-exchange cation in the zeolite's structure, which means that $Na^+$ mainly balances the charge of aluminosilicate framework. The surface morphology of the zeolite Na-P1 is shown in Fig. 2B.

External cation exchange capacity (ECEC) was determined through the indication of the maximum amount of HDTMA-Br attached to the zeolite's surface. For this purpose, 1 g of zeolite grinded in an agate mortar and 100 ml of double-distilled water was mixed with a magnetic stirrer for 3 h at 80 °C. Then, 1 g of dissolved HDTMA-Br was added to the suspension and stirred for a further 24 h at 80 °C. After this period, another portion of HDTMA-Br solution (1 g/100 ml) was added and mixed for 5 h. The zeolite was centrifuged and washed with hot (80 °C) water until the negative reaction occurred for the chlorides. The zeolite was washed with hot ethanol and dried. Using an automatic analyzer CHNS Elementar Vario EL III, the content of nitrogen and the carbon and hydrogen in the solid state were determined. The difference in the content of CHN between Na-P1 zeolite and that treated with HDTMA was used to calculate ECEC. To confirm that after the modification process the surfactant did not crystallize and was attached to the zeolite's surface by ion exchange, XRD has been performed. On the diffraction pattern, peaks derived from HDTMA did not appear (Fig. 1C). Furthermore, as can be seen in the Fig. 2C, the surface morphology did not change.

### 2.2. Modification

The objective was to design a process at low temperature which still effectively modified the zeolite. Another challenge was to reduce the amount of water used by lowering the ratio of the solid state (zeolite) in the solution ($HDTMA_{aq}$). A series of experiments were planned. 50 g of zeolite was placed into a beaker and then saturated with a solution of HDTMA. Depending on the assumed temperature of the process, the mixture has been heated to 40 °C or 60 °C. Various volumes of the HDTMA solution were used, depending on the assumed ratio (Table 1). However, in a given volume, there was always 8.9 g of HDTMA. This amount of surfactant corresponds to one full external cation exchange capacity ECEC (ECEC = 24.4 meq/100 g → 8.9 g of HDTMA/100 g of zeolite). In the case of an assumed room temperature (20 °C) the heating during HDTMA dissolution has been eliminated. The surfactant was dissolved using an ultrasonic disintegrator. It turned out that this method also allows for effective dissolution of HDTMA in a very small amount of water (50 ml).

Following the selection of best conditions, five samples of organo-zeolites were prepared by mixing 50 g of zeolite Na-P1 with 100 g of the HDTMA-Br solution at concentrations of 0.2, 0.4, 0.6, 0.8, 1.0 of ECEC. After 6 h of stirring at room temperature, the samples were centrifuged and dried at 60 °C.

### 2.3. Sorption experiments

All chemicals used in this study (benzene, toluene, p-xylene, and methanol) were of analytical grade. The solubility of the benzene, toluene and p-xylene in water at 20 °C is 0.188, 0.067, and 0.020%, respectively [48]. Therefore, to prevent confrontation with insolubility at higher concentrations, the adsorption of benzene, toluene and xylene were made in the mixture of distilled water