Adsorption of BTX from aqueous solutions by Na-P1 zeolite obtained from fly ash

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ABSTRACT

The adsorption of BTX (benzene, toluene, o- and p-xylene) from aqueous solution by synthetic zeolite Na-P1 obtained from fly ash was examined. The adsorbent was characterized by scanning electron microscope (SEM-EDS) and X-ray diffraction (XRD). Surface area and pore volume distribution were determined using a nitrogen adsorption/desorption isotherm. BTX adsorption tests, including the influence of contact time, sorption isotherms and the influence of initial concentration, were performed in a batch multicomponent system. The sorption capacity followed the order xylene > toluene > benzene, and the removal efficiency decreased with an increase in initial BTX concentration. The process kinetics was evaluated using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The adsorption equilibrium was reached within 24 h and followed pseudo-second-order kinetics. The Langmuir, Freundlich and Temkin models were used to evaluate the adsorption capacity of Na-P1. The Langmuir model was found to be the most suitable for all BTX sorption from a multicomponent system. The calculated maximum adsorption capacities of Na-P1 (q max) for benzene, toluene, o- and p-xylene were 0.032, 0.050, 0.147 and 0.129 respectively.

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1. Introduction

In recent decades, water pollution has become a serious environmental problem as a consequence of progressive industrialization and the development of civilization. Benzene, toluene and xylene (BTX) compounds are some of the most hazardous water contaminants, since they have toxic and carcinogenic properties. Even at very low concentrations, they may adversely affect the biological functions of terrestrial and aquatic ecosystems (Standekar et al., 2009; Tang et al., 2011; Nourmoradi et al., 2012; Szarlip et al., 2014; Szala et al., 2015; Moro et al., 2015); a concentration of 0.01 mg/L may not only significantly alter the flavour of drinking water but also endanger public health. For these reasons, strict limits have been imposed all over the world on their concentrations in water and wastewater, and the removal of BTX has become necessary before water is released into the environment.

The most common sources of BTX water contamination appear to be petroleum leakages from underground storage tanks, pipelines or tankers. Other sources include municipal waste, the petrochemical and chemical industries, the printing and leather industries, rubber manufacture, plastics decomposition, solvent extraction, agricultural effluents, exhaust gases and petroleum leakages during car accidents (Su et al., 2010; Szala et al., 2015; Bandura et al., 2015a).

Many conventional methods can be employed to remove BTX from water and wastewater, including adsorption, aeration, biological oxidation and chemical oxidation. Of these, adsorption processes involving porous solids are the most popular, and are widely utilized in engineering practice since they permit the recovery of these compounds (Lin and Huang, 1999). Various mineral and organo-mineral sorbents have recently been regarded as alternative adsorbents which are potentially useful for the removal of BTX from water (Zytunes, 1994; Sharmasarkar et al., 2000; Standekar et al., 2009; Simpson and Bowman, 2009; Torabian et al., 2010; Aivaloti et al., 2010; Moura et al., 2011; Alejandro et al., 2012; Simantiraki et al., 2012; Nourmoradi et al., 2012; Carvalho et al., 2012; Vidal et al., 2012; Aleghafouri et al., 2015; Szala et al., 2015; Muir and Bajda, 2016; Bandura et al., 2016).

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Zeolites belong to the group of aluminosilicates, with a three-dimensional lattice composed of [AlO4] and [SiO4] tetrahedrons connected by their corners, creating a regular system of channel and chambers. This unique structure provides zeolite minerals with several properties such as ion exchange, molecular sieving and catalytic and adsorption properties. They are therefore widely applied in environmental engineering (Sprynskyy et al., 2005; Franus and Wdowin, 2010; Missalides, 2011; Wdowin et al., 2012; Merrihi and Jalali, 2012; Chałupnik et al., 2013; Perego et al., 2013; Wdowin et al., 2014b; Kryzsl-Komosińska et al., 2015; Bandura et al., 2015b; Woszuk and Franus, 2016). In general, most synthetic zeolites exhibit better sorption and/or catalytic properties than natural ones. They can be obtained using various starting materials such as chemical reagents (Zhang et al., 2015), clay minerals (Ma et al., 2014; Musyoka et al., 2014; Ayele et al., 2015), silicate group minerals (Pichór et al., 2014; Vinaches et al., 2015) or coal combustion byproducts such as fly ash (Querol et al., 1997; Tanaka et al., 2004; Derkowski et al., 2007; Musyoka et al., 2013; Shoumikova and Stoyanova, 2013; Bukhari et al., 2015).

In our previous studies, we reported that zeolites from fly ash are efficient sorbents for the clean-up of land-based petroleum spills and BTX trapping from gas streams (Bandura et al., 2015a, 2016). In this work, we investigate the potential role of zeolite Na-P1 in terms of BTX removal from aqueous solution.

2. Materials and methods

2.1. Adsorbent preparation

The Na-P1 zeolite was obtained using the technological line prototype described by Wdowin et al. (2014a). The following conditions were used during synthesis: 20 kg fly ash, 12 kg NaOH, 90 L water, temperature 80 °C, and duration 36 h. Fly ash was acquired from the Kozienice coal-fired power plant (Poland) (Franus et al., 2015).

2.2. Characterization of the obtained zeolite

Scanning electron microscope images were taken and the chemical composition in microareas was determined using an FEI Quanta 250 FEG microscope equipped with an EDS probe. The mineral composition of the sorbent was determined from powder XRD spectra (2θ from 5° to 65°) registered using a Philips X’pert APD with a PW 3020 goniometer, Cu lamp and graphite monochromator. Nitrogen adsorption/desorption isotherms were measured at −194.85 °C using a Micromeritics ASAP 2020 device. The BET specific surface area, Barret-Joyner-Halenda (BJH) nanopore size distribution functions, the total pore volume at maximum p/p0, and micro pore volume, surface area, and external surface area were estimated from the isotherms by the t-plot method, using ASAP 2020 software provided by the equipment manufacturer. The range of pore size measured was divided into two sub-ranges: micropores (defined as less than 2 nm) and mesopores (2–50 nm).

2.3. Adsorption studies

Analytical-grade benzene, toluene (Chempur), o- and p-xylene (Merc Millipore) and Milli-Q water were used in the adsorption experiments. Adsorption studies were performed using the batch technique. Selected properties of the BTX compound are summarized in Table 1. BTX stock solutions of 200 mg/L (around 50 mg/L of each BTX) were prepared by dissolving the appropriate amount of hydrocarbon in water, and were further diluted to the required concentrations before use. Due to the poor water solubility of BTX compounds, they were dissolved beforehand in a small amount of methanol so that its concentration in the stock solutions did not exceed 1%.

In order to examine the influence of contact time, a multi-solute system of a total BTX concentration of 20 mg/L was used for time intervals ranging from 5 min to 6 h. The uptake of the adsorbate at time t, qe (mg/g), was calculated using the following equation:

\[ qe = \frac{(C_0 - C_t)}{m} \times \text{V} \]

where \( q_e \) is the amount of BTX adsorbed (mg/g) at time t, and \( C_0 \) and \( C_t \) are the initial and equilibrium concentrations of BTX in solution (mg/L) respectively. V is the volume (L) of solution, and m (g) is the mass of adsorbent.

To examine the sorption efficiency and the influence of the initial concentration in a multi-solute system, \( C_0 \) varying from about 1.3 to 20 mg/L for each compound (equivalent to a total BTX concentration of 5–80 mg/L) was used. The time needed to achieve equilibrium of sorption was 24 h. The adsorption capacity, expressed as the amount of BTX adsorbed per gram of adsorbent (mg/g), was calculated as follows:

\[ qe = \frac{(C_0 - C_t)}{m} \times \text{V} \]

The efficiency of BTX adsorption on Na-P1 was calculated from the equation below:

\[ \text{Adsorption efficiency(%) = } \frac{C_0 - C_t}{C_0} \times 100\% \]

where \( q_e \) is the amount of BTX adsorbed (mg/g) at equilibrium, and \( C_0 \) and \( C_t \) are respectively the initial and equilibrium concentrations of BTX (mg/L) in solution. V is the volume (L) of the solution, and m (g) is the mass of adsorbent.

The sorption experiments were performed in closed glass vials using 0.5 g of the adsorbent and 10 mL of BTX solutions. The vials were placed into an SI 500 incubator (Stuart) and shaken at a rate of 175 rpm at a temperature of 20 °C. After a set time, the samples were centrifuged at a rate of 4000 rpm; following this, 2.5 mL of each sample was collected and extracted with dichloromethane (0.5 mL), with 2-fluorotoluene as an internal standard. The samples were left to develop visible separation of the organic and inorganic phases, which were then separated from each other. In order to remove residual water from the organic phase, anhydrous sodium sulphate was added to the organic phase, which was further analysed. All of the experiments were performed in duplicate and included blank samples, in order to eliminate errors connected with concentration losses.

The quantitative analysis of BTX in samples before and after sorption was carried out using gas chromatography (GC Ultra by Thermo Scientific) with a flame ionization detector (FID).

The parameters of the chromatographic analysis were as follows:

- Column: capillary column DB-5MS (30 m, 0.25 mm ID, 0.25 μm).
- Carrier gas: helium 5.0 (Messner), a constant flow of 1.5 mL/min.
- Volume of the dispensed sample: 1 mL.

The temperature was programmed depending on the analysis condition.
2.4. Analysing sorption data

To determine kinetic parameters and analyse the mechanism of adsorption, three different kinetic models were applied: the Lagergren model, also referred to as pseudo-first-order (Gupta et al., 2003), a pseudo-second-order model (Ho and McKay, 1999) and an intraparticle diffusion model (Weber and Morris, 1964).

The pseudo-first-order model equation is represented by:

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]

and can be expressed in the following linearized form:

\[
\log(q_t - q_e) = \log q_e - \frac{k_1}{2.303} \cdot t
\]

where \( k_1 \) is the Lagergren rate constant of adsorption (L/min), and \( q_t \) (mg/g) and \( q_e \) (mg/g) are the quantities of the adsorbed substance at equilibrium and at time \( t \) respectively. This equation is often used to interpret experimental data; however, in practice it shows large deviations in fitting procedures.

The pseudo-second-order model was proposed by Ho and McKay (1999) and is currently the most widely used kinetic equation:

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2
\]

which can also be expressed in the following linearized form:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t
\]

where \( k_2 \) is the pseudo-second-order rate constant of adsorption (g/(mg min)). The values of \( q_e \) and \( k_2 \) were determined from the slope and intercept of the plots of \( t/q_t \) vs. \( t \).

The Weber and Morris model of intraparticle diffusion assumes that the adsorption varies linearly with the square of the contact time. It is expressed by the following equation:

\[
q_t = K_d \cdot t^{0.5} + C
\]

where \( K_d \) is the rate constant of intraparticle diffusion (mg/(g min^{0.5})), \( t^{0.5} \) is the square root of the time, and \( C \) is the intercept related to the thickness of the boundary layer.

If the plot \( q_t \) vs. \( t^{0.5} \) is linear and passes through the origin, the main rate-limiting step for the adsorption is intraparticle diffusion process. When the relationship \( q_t \) vs. \( t^{0.5} \) does not pass through the origin and/or is non-linear, the sorption process is accompanied by other mechanisms (Moura et al., 2011).

The Langmuir (1916), Freundlich (1906) and Temkin (Temkin and Pyzhov, 1940) isotherm models were applied to the experimental sorption equilibrium data. The parameters of the isotherm equations for these processes were calculated by regression using the linear form of the isotherm equations.

The Langmuir isotherm is based on the assumption that adsorption takes place at specific homogeneous sites on the surface of the adsorbent, without significant interaction between the adsorbed species. A single layer of adsorbed molecules is formed on the adsorbent surface. The linearized Langmuir isotherm is represented by the following equation:

\[
\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m}
\]

where \( C_e \) is the solute concentration at equilibrium (mg/L), \( q_e \) is the adsorption capacity at equilibrium (mg/g), \( K_L \) is the Langmuir adsorption constant (L/mg), and \( q_m \) is the maximum amount of adsorbate covering the sorbent surface (monolayer capacity) (mg/g).

The parameters \( q_m \), \( K_L \) and correlation coefficient \( R^2 \) are determined by linear regression from the relationship \( C_e/q_e \) vs. \( C_e \). The essential characteristics of the Langmuir isotherm can be characterized by a separation factor or equilibrium constant, \( R_L \), which is defined as:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

Values between 0 and 1 of the separation factor (\( R_L \)) indicate the suitability of the process (Chen et al., 2011).

The Freundlich model can be applied to non-ideal systems, including multilayer adsorption processes on heterogeneous surfaces, and is expressed by the following equation:

\[
q_e = K_F C_e^{1/n}
\]

where \( C_e \) is the solute concentration (mg/L) at equilibrium, \( q_e \) is the adsorption capacity (mg/g) at equilibrium, and \( K_F \) [(mg/g)/(L/mg)^n] and \( n \) are the Freundlich adsorption isotherm constants related to the saturation capacity and intensity of adsorption respectively.

The parameters \( K_F \) and \( 1/n \) and the correlation coefficient \( R^2 \) are determined by linear regression from the relationship \( q_e \) vs. \( \log C_e \). It is known that \( 1/n \) values of between 0.1 and 1 (for \( n \) between 1 and 10) indicate favourable adsorption (Vidal et al., 2011). Lower values of \( n \) suggest unfavourable conditions for adsorption and the possibility of competitive adsorption.

The Temkin model considers the effects of indirect adsorbate–adsorbate interactions on adsorption isotherms, and assumes that heats of adsorption will more often decrease
than increase with increasing coverage. This equation has the form:

\[ q_e = \frac{RT}{b} \ln \left( A \cdot C_e \right) \]

where \( T \) is the absolute temperature (K), \( R \) is the gas constant, \( A \) is the Temkin isotherm constant (L/g), \( b \) is the Temkin constant related to the heat of sorption (kJ/mol) and \( C_e \) is the equilibrium concentration (mg/L). The parameters \( A \) and \( b \) and the correlation coefficient \( R^2 \) were determined by linear regression from the relationship \( q_e \) vs. \( \ln C_e \).

3. Results and discussion

3.1. Characterization of the adsorbent

The morphology and chemical composition of the individual mineral phases in microareas measured by SEM-EDS are shown in Fig. 1.

Zeolite Na-P1 occurs in the form of pillars, with characteristic rosette blends of sizes usually exceeding 10 mm. Microprobe chemical analysis shows that the main cation balancing the charge of the aluminosilicate lattice is sodium. The zeolite phase content in Na-P1 was evidenced by the main d-spacings \( d_{d Haley} \) of 7.10, 5.01, 4.10 and 3.18 Å (Fig. 2). In addition to the main zeolitic phase, mullite, quartz and trace amounts of calcite were detected. Moreover, the slight hump observed in the angle in the range 20–40° (2θ) in the XRD spectra can be attributed to the presence of an amorphous silica phase.

Fig. 3 shows the nitrogen adsorption–desorption isotherm at −194.85 °C and the BJH mesopore size distribution curve determined from the desorption branch of the isotherm. The adsorption branch of the presented isotherm belongs to type IV, according to the IUPAC classification (Carmody et al., 2007). The hysteresis loop (observed in a p/p_0 range of between 0.46 and 0.99) and its shape indicates a high contribution from mesopores. This corresponds most closely to the
Fig. 3 – Nitrogen adsorption/desorption isotherm and BJH nanopore size distribution of Na-P1.

Fig. 4 – Multicomponent adsorption kinetics of BTX. Conditions: 0.5 g of Na-P1, 10 mL of BTX solution, \( C_0 = \) around 5 mg/L of each compound (20 mg/L in total), \( T = 20^\circ C \).

H3 and B types, according to the IUPAC and de Boer classifications respectively. These types are characteristic for solids with slit-shaped pores (plates or faced/edge particles such as cubes) of uniform or non-uniform size or shape, which is typical for zeolites (Leo-fanti et al., 1998). Some papers also report the presence of ink-bottle type pores; in this case, similar hysteresis loops were categorized as type H2 (Sprynsky et al., 2005; Kim and Ahn, 2012). Mesopore size distribution is homogenous, with a maximum at 4 nm. Table 2 summarizes the nitrogen adsorption/desorption data. The textural parameters reveal the mesoporous character of Na-P1 zeolite.

3.2 Adsorption studies

3.2.1. Influence of contact time and sorption kinetics

The effect of the contact time on the removal of BTX at a \( C_0 \) of 20 mg/L is presented in Fig. 4. The sorption increased rapidly at the initial stage of sorption (over the first hour) due to a large number of vacant active sites. With time, the diminishing availability of the remaining active sites and the formation of repulsion between adsorbate molecules leads to a decrease in adsorption rate (Mall et al., 2006; Yousef et al., 2011; Li et al., 2012) reflected by the plateau line indicating the equilibrium state (after about 24 h). Accordingly, a contact time of 24 h was used in the adsorption isotherm studies. At equilibrium, zeolite Na-P1 removed around 35% of benzene, 55% of toluene, 77% of o-xylene and 99% of p-xylene, corresponding to

<table>
<thead>
<tr>
<th>BTX</th>
<th>( C_0 ) (mg/L)</th>
<th>( q_e ) (mg/g)</th>
<th>( k_1 ) (1/h)</th>
<th>( R^2 )</th>
<th>( k_2 ) (g/mg h)</th>
<th>( R^2 )</th>
<th>( b ) (mg/(g h))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzeno</td>
<td>5.86</td>
<td>0.031</td>
<td>0.028245</td>
<td>0.978</td>
<td>0.096</td>
<td>0.039</td>
<td>0.04384</td>
<td>0.882</td>
</tr>
<tr>
<td>Toluene</td>
<td>4.84</td>
<td>0.053</td>
<td>0.050943</td>
<td>0.999</td>
<td>0.0214</td>
<td>0.0206</td>
<td>0.0426</td>
<td>0.949</td>
</tr>
<tr>
<td>P-Xylene</td>
<td>5.52</td>
<td>0.027</td>
<td>0.0225</td>
<td>0.981</td>
<td>0.0202</td>
<td>0.018</td>
<td>0.0792</td>
<td>0.997</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>5.22</td>
<td>0.027</td>
<td>0.0225</td>
<td>0.981</td>
<td>0.0202</td>
<td>0.018</td>
<td>0.0792</td>
<td>0.997</td>
</tr>
</tbody>
</table>

where:
- \( C_0 \)—the initial concentration, \( q_e \)—equilibrium sorption capacity, \( k_1 \)—equilibrium sorption capacity calculated from the PFOE/PSOE, \( k_2 \)—rate constant for PSOE, \( K_{f} \)—rate constant for PFOE, \( K_{d} \)—intraparticle diffusion rate constant proportional to the boundary layer thickness in the area a or b.
the maximum adsorption uptake under the applied operating conditions.

The parameters of the pseudo-first-order, pseudo-second-order and intraparticle diffusion models for BTX adsorbed by Na-P1 are summarized in Table 3. Fig. 5(a)–(c) presents the analysed model plots for experimental data. The R² values derived from the pseudo-first-order model were relatively small, and varied from 0.826 to 0.978. Moreover, the calculated qₑ values did not agree with the experimental ones, showing that the adsorption of BTX on the Na-P1 zeolite is not a first-order reaction. The correlation coefficients R² of almost 1.00 confirm that the adsorption processes followed pseudo-second-order kinetics. Values of qₑ calculated from the pseudo-second-order model corresponded well with experimental data. In addition, the plots in Fig. 5(b) exhibit a linear relationship, indicating the applicability of the pseudo-second-order model. Larger k₂ values indicate that the adsorption of benzene and toluene required a shorter time to achieve a specific fractional uptake than xylene. A pseudo-second-order model suggests that adsorption involves a chemisorption process in addition to physisorption. The chemisorption may be the rate-limiting step where valency forces are involved via electron-sharing or exchange between the adsorbent and the adsorbate (Ho and McKay, 1999). The key driving force for the adsorption is the difference in the adsorbed concentration of adsorbate at equilibrium (qₑ) and at time t (qₜ), and the adsorption capacity is proportional to the number of active adsorption sites on the adsorbent (Alshameri et al., 2014).

There are three steps involved in the sorption process: (1) transport of sorbate molecules from the boundary film to the external surface of the sorbent (film diffusion); (2) transfer of sorbate from the surface to the intraparticular active sites (particle diffusion); and (3) adsorption of sorbate by the active sites of adsorbent (Pan et al., 2011; Abdelwahab and Amin, 2013; Liao et al., 2013; Nešić et al., 2013; Alshameri et al., 2014). To determine the relative contributions of surface and intraparticle diffusion to the sorption kinetics, the Weber–Morris model was applied. The plots qₑ vs. t⁰.5 do not pass through the origin, meaning that intraparticle diffusion was not the sole rate-limiting step. Two steps were involved in the sorption process, as shown in Fig. 4(c): (a) the initial step represented by the steep linear plot associated with surface diffusion (external surface adsorption); and a second step (b) represented by the less steep plot associated with the gradual sorption of adsorbates, wherein the intraparticle diffusion was the rate-limiting step. The slope of the line at stages (a) and (b) is denoted as the rate parameters Kida and Kidb respectively (Table 3). The data show that the order of the adsorption rate was Kida > Kidb for each compound. The values of intercept C provide information about the thickness of the boundary layer; the resistance to the external mass transfer increases as the intercept increases (Alshameri et al., 2014). The thickness of the boundary layer followed the order Cₐ > Cₑ, confirming that surface diffusion plays a more important role in BTX adsorption onto Na-P1.

Usually, transport in the bulk phase is a main factor determining sorption rate in systems with poor stirring, low adsorbate concentration, small sizes of adsorbate molecules and high affinity of adsorbate for the adsorbent. In contrast, intraparticle diffusion is the main factor in the kinetics of adsorption systems which are characterized by a high concentration of adsorbate, good stirring, large sizes of adsorbate molecules and a low affinity of the adsorbate for the adsorbent.

Pseudo-second-order kinetics has also been reported for the sorption of BTX and other benzene derivatives onto unmodified natural zeolite (Yousef et al., 2011; Simantiraki et al., 2012), natural and synthetic ones modified with surfactant (Seifi et al., 2011; Vidal et al., 2012), lignite (Aivalioti et al., 2012), Luffa cylindrica fibre (Abdelwahab and Amin, 2013), graphene (Li et al., 2012), biomass (Costa et al., 2012), sewage sludge and municipal solid waste compost (Simantiraki et al., 2013).

3.2.2. Influence of initial concentration and sorption isotherms

Fig. 6 shows BTX removal efficiency (%) and sorption capacity (mg of adsorbate per 1 g of adsorbent) for different initial concentrations. The highest adsorption was noted for xylenes and the lowest for benzene. As can be observed, increasing the initial concentration resulted in a decrease of the BTX removal (%), and this may be related to saturation of the adsorption sites at higher BTX concentrations. Simultaneously, the amount of BTX adsorbed per 1 g of zeolite increased. The initial BTX concentration provides a driving force to overcome mass transfer resistance. As a result, a higher initial concentration tends to enhance the adsorption capacity (Abdelwahab and Amin, 2013). Simantiraki et al. (2012) observed a similar depen-
tendency for the adsorption of BTEX onto compost and natural Greek zeolite.

Based on the experimental data, the adsorption of BTEX onto zeolite Na-P1 followed the order xylene > toluene > benzene, as reported for lignite (Aivalioti et al., 2012), diatomite (Aivalioti et al., 2010) and organically modified minerals such as montmorillonite (Nourmoradi et al., 2012), zeolite Y (Vidal et al., 2012) and smectite (Carvalho et al., 2012). Presumably, this order corresponds to the descending order of hydrophobicity and molecular weight and ascending order of water solubility of BTEX compounds (Table 1). However, Torabian et al. (2010) observed an opposite order of BTEX sorption onto organically modified zeolite, which was attributed to the partitioning mechanism. According to this assumption, the investigated sorbents showed a higher adsorption capacity for smaller molecules with lower spatial hindering effects.

The adsorption isotherms are presented in Fig. 7. The adsorption parameters determined by fitting the experimental data to the Langmuir, Freundlich and Temkin models are given in Table 4.

Table 4 – Sorption parameters determined from the Langmuir, Freundlich and Temkin isotherm models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Benzene</th>
<th>Toluene</th>
<th>p-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td>0.038</td>
<td>0.050</td>
<td>0.129</td>
<td>0.147</td>
</tr>
<tr>
<td>Qmax [mg/g]</td>
<td>0.706</td>
<td>1.069</td>
<td>1.473</td>
<td>1.209</td>
</tr>
<tr>
<td>K Langmuir [L/mg]</td>
<td>0.067–0.517</td>
<td>0.043–0.402</td>
<td>0.036–0.356</td>
<td>0.038–0.373</td>
</tr>
<tr>
<td>R²</td>
<td>0.989</td>
<td>0.998</td>
<td>0.998</td>
<td>0.998</td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.014</td>
<td>0.024</td>
<td>0.059</td>
<td>0.063</td>
</tr>
<tr>
<td>Kf [mg/g][L/mg]¹/n</td>
<td>2.699</td>
<td>3.681</td>
<td>2.860</td>
<td>2.830</td>
</tr>
<tr>
<td>n</td>
<td>0.739</td>
<td>0.768</td>
<td>0.963</td>
<td>0.964</td>
</tr>
<tr>
<td>R²</td>
<td>0.963</td>
<td>0.998</td>
<td>0.997</td>
<td>0.997</td>
</tr>
<tr>
<td><strong>Temkin</strong></td>
<td>317.420</td>
<td>296.615</td>
<td>113.121</td>
<td>99.309</td>
</tr>
<tr>
<td>A [L/g]</td>
<td>0.818</td>
<td>0.860</td>
<td>0.997</td>
<td>0.997</td>
</tr>
<tr>
<td>R²</td>
<td>0.998</td>
<td>0.963</td>
<td>0.964</td>
<td>0.964</td>
</tr>
</tbody>
</table>

Fig. 6 – BTEX removal efficiency (%) (a) and sorption capacity (mg BTEX per 1 g of adsorbent) according to the initial concentration. Conditions: 0.5 g of Na-P1, 10 mL of BTEX solution, C0 = 1.3–20 mg/L of each compound (around 5–80 mg/L in total), T = 20 °C.

Fig. 7 – Adsorption isotherms of BTEX. Conditions: 0.5 g of Na-P1, 10 mL of BTEX solution, C0 = 1.3–20 mg/L of each compound (around 5–80 mg/L in total), T = 20 °C.

possesses some carbon traces originating from unreacted coal. The values of n suggest favourable adsorption. Values of the constant b for xylenes were much lower than for benzene and toluene, which may be attributed to a higher degree of surface coverage. One can notice a relationship between b (degree of coverage) and the sorption capacity. A higher b value corresponds to smaller sorption capacity, expressed as mg of compound per 1 g of sorbent.

Several studies report similar results for the sorption capacities of mineral and organo-mineral sorbents towards BTEX compounds. Aivalioti et al. (2010, 2012) studied the sorption of benzene, toluene and xylenes from aqueous solution onto diatomite and lignite, and found that the Freundlich and pseudo-second-order models fitted the exper-
minal data well. The values of sorption capacities for BTX compounds were in the range 0.1–0.38 mg/g for untreated diatomite and increased up to 0.8 mg/g for diatomite calcined at 750 °C. In the case of lignite, the sorption capacity was about 0.08 mg/g for benzene, 0.14 mg/g for toluene and 0.20–0.25 mg/g for xylenes. In our study, the sorption capacity, expressed as the sum of BTX sorbed per 1 g of zeolite Na-P1, was about 0.34 mg/g. Surface modifications using quaternary ammonium salts may improve the initial sorption capacities of mineral sorbents towards BTX compounds as described recently [Nourmoradi et al., 2012; Vidal et al., 2012; Szala et al., 2015]. However, this involves the problem of toxic derivatives of some ammonium salts.

4. Conclusions

In this paper, synthetic zeolite Na-P1 obtained from fly ash from a hydrothermal conversion process was studied in terms of BTX sorption from aqueous solutions. Sorption equilibrium was reached after 24 h. The kinetics results revealed that the pseudo-second-order model best described the adsorption of BTX onto Na-P1 with a correlation coefficient equal to 1. Furthermore, according to Weber and Morris model plots, the sorption process involved two stages: surface and intraparticle diffusion. The sorption capacities increased in the order benzene → toluene → xylenes, and the efficiency of removal decreased with an increase of BTX initial concentration. The most suitable model describing sorption equilibrium was the Langmuir isotherm, with high R² coefficients for all compounds investigated. Na-P1 zeolite may constitute a prospective low-cost and environmentally friendly sorbent for BTX removal, and may be considered as a substitute for other mineral sorbents under certain conditions, or as a filling material for permeable reactive barriers.

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References


