REMOVAL OF ENVIRONMENTAL POLLUTIONS USING ZEOLITES FROM FLY ASH: A REVIEW

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ABSTRACT

The paper presents the possibilities of using synthetic zeolites in environmental protection and engineering. As a result of the synthesis reaction of fly ash, the following types of zeolites were obtained: Na-X, Na-P1, sodalite, and two mixtures of zeolites composed of Na-P1/Na-X/Linde-A and Na-P1/Linde-A. Obtained zeolites were tested on the removal of ammonium ions from water, radionuclides (226Ra and 228Ra) from mine water, zinc ions from washing baths, CO₂ from exhaust gases, and oil refining. In the case of ammonium ion removal, the uptake of these ions from aqueous solutions increases with the increase in the initial concentration of NH₄⁺ in the tested artificial solution. The tests of radionuclides removal have shown high efficiency that reached 98%. The analysis of purification washing baths results indicate Zn²⁺ high removal efficiency of the tested zeolite. Zeolites are a bit less effective at removing CO₂. However, they were very good materials in oil refining where the obtained results are slightly better than for the adsorbents used commercially for this purpose. The results showed that, in most cases, the zeolites tested remove the aforementioned contaminants very effectively, and are a competing material for various kinds of commercially available adsorbents used for the described impurities.

KEYWORDS: synthetic zeolites, ammonium ions, radionuclides, oil refining, carbon dioxide, washings bath

1. INTRODUCTION

Zeolites are microporous, hydrated aluminosilicates of alkali elements, alkaline earth metals or other cations which, in their crystal structure, contain numerous channels and chambers of various sizes (in the order of several angstroms), resulting in a number of sorption, ion exchange, molecular-sieve and catalytic properties [1-4]. Because of these properties, they are widely used in many branches of industry, agriculture, medicine, chemical technology, environmental protection, and engineering [4-8]. They are used, among other things, in reactions with organic compounds (the separation of unsaturated hydrocarbons and removal of petroleum substances [9] by means of selective adsorption, as well as other organic substances using molecular sieve properties, they are also used for the treatment of acidic wastewaters generated by the production of monochloroacetic acid containing chlorinated organic compounds [10] as well as BTX [11] or phenol removal from wastewaters [12], as membranes and molecular sieves in gaseous pollutions removal, in wastewaters treatment, and in nuclear industry. They are good ion exchangers, and therefore they are used as gas separators, and in medicine [13].

Considering environmental protection, zeolites are generally used in water and wastewater treatment technologies as well as in the purification of flue gases.

With regard to wastewater treatment, they have the ability to capture a large number of ions that constitute pollution, including radionuclides, such as 137Cs and 60Sr [14], as well as heavy metals, ammonium ions, chloroform, carbon tetrachloride from wastewaters and acidic mine waters.

For removal of ammonium ions, both synthetic zeolites, such as Na-P, Na-Y [15], 4A-X, Na-P1, Na-chabazite, KM, analcime, sodalite [4, 16, 17], 13X [18], and natural zeolites, mainly clinoptilolite [15, 19, 20, 21, 22], were studied.

Regarding heavy metal sorption, zeolites exhibit a distinct selectivity for this type of contaminants present in water, wastewaters or wastewater sludge [23, 24].

For analyses of removing heavy metals from contaminated water that is rich in iron and aluminum, according to Qerol et al. [4], synthetic zeolites show very good selectivity presented in the following order: Fe³⁺>Al³⁺>Cu²⁺≥Pb²⁺≥Cd²⁺≥Ti⁺>Zn²⁺>Mn²⁺>Ca²⁺>Sr²⁺>Mg²⁺. Lee et al. [25] analyzed the selective sorption of cations Zn, Cu, Cd, and Pb for natural and synthetic zeolites. The results showed that synthetic zeolites exhibit higher cation exchange capacity and, hence, a larger amount of adsorption of heavy metal cations.

Zeolites, among other low-cost sorbents, are widely used in the purification of soil [26], gas [27, 28], and aqueous
solutions from mercury pollution [29, 30]. A synthetic zeolite impregnated with silver resistant to high temperatures was created for the capture of mercury from flue gases [28]. In addition, this zeolite had a high selectivity with regard to dioxins, furans and other polycyclic hydrocarbons, which, after initial evaporation of mercury, are subjected to thermal decomposition [10].

However, when it comes to the purification of flue gases, zeolites turned out to be best at removing the following pollutants: SO2, CO2, CO, NOx, H2S, NH3 and Hg [28, 31].

The main objective of this paper is to determine how useful synthetic zeolites obtained from fly ash can be when it comes to the removal of environmental pollutants, i.e. the removal of ammonium ions from aqueous solutions, radionuclides from mine water, and zinc from washing baths, and how they can be used in oil refining, and removal of CO2 from exhaust gases. Some sources indicated the application of fly ash in such cases [32], but zeolites have much better surface properties, necessary to remove the aforementioned pollutants.

The article presents the results of an examination carried out by the authors as compared with the results obtained by others.

2. MATERIALS AND METHODS

2.1. Research materials

For the purpose of environmental examination, we used synthetic zeolites that were obtained by reaction of fly ash with NaOH under different conditions (i.e. the concentration of NaOH, time and temperature of reactions). The synthetic zeolite materials were Na-X, Na-P1, sodalite, which were the result of the conversion of fly ash in the laboratory scale, as well mixtures of Na-P1/Na-X/Linde-A and Na-P1/Linde-A produced on the basis of a prototype production line for zeolite synthesis [33].

2.2. Synthesis conditions

The extent of fly ash conversion into zeolite materials is dependent on the conditions of the synthesis. The scheme of the process is shown below [34]:

\[ \text{fly ash} + x \text{ mol dm}^{-3}\text{NaOH} \xrightarrow{\text{time}} \frac{\text{temperature}}{\text{zeolite}} + \frac{\text{residuum}}{\text{residuum}} \]

Conditions for the synthesis of various types of zeolites and mixtures are as follows:

- **Synthesis of Na-X phase**: 20 g of fly ash was mixed with 0.5 dm³ of NaOH at a concentration of 3 mol*dm⁻³ for 24 h at 75 °C;
- **Synthesis of Na-P1 phase**: 20 g of fly ash was mixed with 0.5 dm³ of NaOH at a concentration of 3 mol*dm⁻³ for 24 h at 95 °C;
- **Synthesis of sodalite phase**: 20 g of fly ash was mixed with 0.8 dm³ of NaOH at a concentration of 5 mol*dm⁻³ + 0.4 dm³ of NaCl at a concentration of 3 mol*dm⁻³ for 24 h at 95 °C;
- **Synthesis of Na-P1 phase**: 20 kg of fly ash, 12 kg NaOH, 90 dm³ of water, the reaction temperature of 80 °C and time of reaction is 36 h;
- **Synthesis of Na-P1/Na-X/Linde-A mixtures**: 15 kg of fly ash, 12 kg NaOH, 90 dm³ of water, the reaction temperature of 80 °C and time of reaction is 24 h;
- **Synthesis of Na-P1/Linde-A mixtures**: 20 kg of fly ash, 12 kg NaOH, 90 dm³ of water, the reaction temperature of 70 °C and time of reaction is 24 h.

2.3. Methodology

This chapter describes the methodology of synthetic zeolites examinations and characteristics as well as methods for the removal of environmental pollutants by zeolites, i.e. removal of ammonium and zinc ions, radionuclides, and CO2 and oil refining.

2.3.1. The phase composition of the analyzed synthetic zeolites and their physico-chemical properties

The obtained zeolite materials were examined by means of X-ray phase analysis (XRD), scanning electron microscopy (SEM) as well as chemical analysis.

The mineral composition of synthetic zeolites was determined via powder XRD using a Philips X’pert APD with PW 3020 goniometer, Cu lamp and graphite monochromator from 5 to 65° 2θ.

The scanning electron microscopy analysis was carried out using an electron microscope - FEI Quanta 250 FEG SEM, equipped with a chemical composition analysis system based on energy dispersion scattering EDS-EDAX.

The cation exchange capacities (CEC) were determined on the basis of the amount of Ba²⁺ ions saturated in the samples and desorbed by 1 mol·dm⁻³ of MgCl₂, where this procedure is recommended by the Association Internationale Pour L’Etude Des Argiles [35].

The specific surface area was determined based on the shape of the vapor nitrogen adsorption/desorption isotherm at -196.15 °C, based on the BET multilayer adsorption theory [36] at p/p₀ between 0.06 and 0.3 (p and p₀ are the equilibrium and saturation pressure of nitrogen, respectively). It was examined on an ASAP 2020 Micromeritics analyzer.

2.3.2. Methodology of ammonium ions removal

The sorption of NH₄⁺ ions on zeolite adsorbents was performed using the batch method. Samples of 0.5 g mass of sorbent were mixed with 50 cm³ of ammonium-rich solution. The initial concentration of NH₄⁺ varied from 15 to 105 mg·dm⁻³. The solutions with zeolite samples were shaken for 60 min, and then centrifuged for 10 min at 3000 rpm. After centrifugation, in the solutions, ammonia nitrogen was de-
determined using a Flow Injection Analyser FIAstar 5000 (FOSS).

The content of NH$_4^+$ ions was calculated according to the following equation:

\[
q_t = \frac{(C_0 - C_e)V}{M}
\]

where, \(q_t\) is the total amount of adsorbed NH$_4^+$ ions [mg·g$^{-1}$], \(C_0\) is the initial concentration of NH$_4^+$ in the solution [mg·dm$^{-3}$], \(C_e\) is the equilibrium concentration of NH$_4^+$ in the solution [mg·dm$^{-3}$], \(V\) is the volume of the analyzed solution [dm$^3$], and \(M\) is the adsorbed mass [g].

The sorption of NH$_4^+$ ions on the tested zeolites was analyzed using the Langmuir and Freundlich isotherm models. For linear Langmuir equation, the following procedure was used:

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}
\]

where, \(q_e\) is the equilibrium amount of NH$_4^+$ exchange by tested zeolites [mg·g$^{-1}$], \(C_e\) is the equilibrium NH$_4^+$ concentration in the solution [mg·dm$^{-3}$], \(q_{max}\) is the maximum uptake of ammonium exchanged [mg·g$^{-1}$], and \(K_L\) is the Langmuir constant [dm$^3$·mg$^{-1}$].

For linear model of Freundlich, the following equation was used:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where, \(K_F\) is the Freundlich constant [dm$^3$·g$^{-1}$], and \(\frac{1}{n}\) is the heterogeneity factor.

### 2.3.3. Methodology of oil refining

In the oil refining test, two oils were used, i.e. TRAFO (transformer) oil and TU-46 (turbine) oil. The process of refining by contact method was performed using the following parameters: the quantity of sorbent about 5% by mass; contact time of 30 min; process temperature 50 °C for TRAFO oil and 70 °C for turbine oil.

The temperature differences result from the differences in viscosity of these oils. While analyzing refined oil, the refining effect was determined based on the calculation of activity index. The activity index was designated from the change in the acid number of the oil before and after refining it, and the bleeding effect was determined by measuring the color intensity of the oil before and after refining. Then, the acid number was defined by means of a photocolorimeter "Spekol". The acid number was determined by the following standard PN-85/C-04066 [37].

The measurement of light extinction in the tested oils was made at selected wavelengths of light (0.455 nm), so that the permeability of the material (T%) of refined used oil was 40%.

The refining effect (determined from the degree of oil bleaching) was calculated using the following equation:

\[
R[\%] = \frac{(E_{raw} - E_{raf})}{E_{raw}} \times 100%
\]

where, \(R\) is the degree of lightening sample; \(E_{raw}\) is the extinction of neat material sample; and \(E_{raf}\) is the extinction of refined oil samples.

The refining effect (determined based on the activity index) was calculated according to the following equation:

\[
W[\%] = \frac{(LK_{raw} - LK_{raf})}{LK_{raw}} \times 100%
\]

where, \(W\) is the activity index; \(LK_{raw}\) is the acid number of the neat material sample; and \(LK_{raf}\) is the acid number of refined oil samples.

### 2.3.4. Methodology of radionuclides removal

The effectiveness of zeolite sorbent with regards to radionuclide removal was measured in an experiment performed at dynamic conditions. In order to obtain a suitable flow-rate of mine water through the bed, the column of about 30 cm in diameter was filled with 26 kg of sand and 2 kg of zeolite.

The mine water to be purified in the experiment came from a hard coal mine KWK Piast from the horizon of 650 m, and contained the following concentrations of isotopes: 226Ra $4.216 \pm 0.534$ [kBq·m$^{-3}$], 228Ra $7.81 \pm 1.46$ [kBq·m$^{-3}$]. Thermal conductivity was 119000 μS·cm$^{-1}$ and salinity 110 g·dm$^{-3}$.

**TABLE 1 - The chemical composition of mine water from KWK Piast.**

<table>
<thead>
<tr>
<th>Element</th>
<th>amount in [mg·dm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>2970</td>
</tr>
<tr>
<td>Magnesium</td>
<td>4410</td>
</tr>
<tr>
<td>Sodium</td>
<td>49700</td>
</tr>
<tr>
<td>Potassium</td>
<td>755</td>
</tr>
<tr>
<td>Ferrum</td>
<td>0.40</td>
</tr>
<tr>
<td>Manganese</td>
<td>4.43</td>
</tr>
<tr>
<td>Barium</td>
<td>0.10</td>
</tr>
<tr>
<td>Strontium</td>
<td>67.2</td>
</tr>
<tr>
<td>Boron</td>
<td>14.8</td>
</tr>
<tr>
<td>Zinc</td>
<td>1.46</td>
</tr>
<tr>
<td>Copper</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.14</td>
</tr>
<tr>
<td>Chlorides</td>
<td>93800</td>
</tr>
<tr>
<td>Sulfates</td>
<td>3690</td>
</tr>
</tbody>
</table>

120 dm$^3$ of salt water was passed through the column. In the examinations of the level of radionuclides removal, the method for the determination of radium isotopes in mine waters using the technique of liquid scintillators was applied. It allows the determination of $^{226}$Ra and $^{228}$Ra; however, the double measurement of the concentrations of radium isotopes in the samples subjected to appropriate preparative work is necessary. The first measurement was taken 24 h after the preparation in order to determine preliminarily the effectiveness of purification, and the second after 30 days.
The method allows for simultaneous determination of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ in water samples. The determination was preceded with chemical preparation, during which radium isotopes were precipitated with a barium carrier in the form of finely-crystalline radium-barium sulfate. The resulting precipitate was mixed with liquid gelling scintillation, which ensures homogeneity of the sample, and radium content was measured in the Quantulus liquid scintillation spectrometer.

### 2.3.5. Methodology of zinc ions removal

In order to evaluate the efficiency of zinc ions removal from the washing baths, synthetic Na-P1 zeolite material was selected. The process of zinc ions uptake was conducted under static and dynamic conditions.

Washing baths used for testing came from the production line of "PZL Swidnik". The washing baths were collected from the bath tube of galvanizing process. The chemical composition of washing baths was as follows: zinc – 47.85 mg·dm$^{-3}$, potassium - 123 mg·dm$^{-3}$, sodium – 10.31 mg·dm$^{-3}$, boron – 3.48 mg·dm$^{-3}$, vanadium – 3.47 mg·dm$^{-3}$, calcium – 1 mg·dm$^{-3}$, aluminum – 0.26 mg·dm$^{-3}$, and magnesium – 0.2 mg·dm$^{-3}$.

The experiment of removing zinc ions by the Na-P1 zeolite was performed under dynamic conditions (in a glass column with a diameter of 1 cm and a height of 50 cm, where the thickness of the bed was 20 cm) and static conditions (in a polypropylene vessel with a volume of 1 dm$^3$).

The maximum exchange capacity "Ac" is the amount of ions that can be exchanged in a column with a bed in specific process conditions. It corresponds to the total removal of the washing area from the column when the ion exchanger contained in the bed is in equilibrium with the solution that is fed to the column. It is calculated with the following equation:

$$ A_c = \frac{(V_0 + 0.5 \cdot \Delta V) \cdot C}{S \cdot L} $$

where, $V_0$ is the volume of the leakage to the point of breakdown [cm$^3$]; $\Delta V$ is the volume of leakage corresponding to the elution from the column of the work zone [cm$^3$]; $C$ is the initial concentration of the solution [mval/cm$^3$], $S$ is the area of bed cross-section [cm$^2$], $L$ is the height of the bed in the column [cm].

The working exchange capacity "Ad" of the bed is the amount of ions that can be exchanged through the bed at the time of breakdown, and it is determined by the following equation:

$$ A_d = \frac{V_0 \cdot C}{S \cdot L} $$

The exchange capacity to the point of breakdown is characterized by such a state of ion exchanger exhaustion, in which the work zone remains almost entirely in the bed. The volume of breakdown "$V_p$" of the bed is determined when the amount of removed ions in the leakage is equal to the permissible amount [38], and the volume saturation "$V_n$" of the bed is determined when the concentration of heavy metals in the effluent reaches baseline value [39]. In order to determine the volume of leakage, a so-called bed volume is very often used, where it is assumed that the bed volume of the ion exchange column constitutes the volume unit [40].

The initial and final concentration of metals in solution was determined by ICP-MS methods using a spectrometer ICP-OES (JOBINYWON U-238).

The amount of metal removed from the solution was calculated from the difference in the concentrations of metal ions in the solution before the ion exchange process (initial concentration) and after the exchange process [41, 42] according to the following equation:

$$ Q = \frac{(C - C_{eq}) \cdot V}{W} $$

where, $Q$ is the amount of metal ions removed by an ion exchanger mass [mval·g$^{-1}$]; $C$ is the initial concentration of the metal solution [mval·dm$^{-3}$]; $C_{eq}$ is the concentration of metal after ion exchange process [mval·dm$^{-3}$]; $V$ is the volume of solution [dm$^3$]; and $W$ is the mass of mineral [g].

### 2.3.6. Methodology of CO$_2$ removal

CO$_2$ sorption measurements were made using an analyzer for precise measurements of physical sorption as well as chemisorption, equipped with an additional device to vapor sorption, and a mass spectrometer - AUTOSORB-1-C (Quantachrome Instruments, USA). Before the measurements, samples were rinsed with helium and calcinated at 373.15 °K during a 4 h period. The scope of works included the appointment of CO$_2$ adsorption isotherms at the temperature of 273 °K.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characteristics of zeolite materials

When applying conversion process variables, the reaction temperature, substrate concentration, the relative proportions between the amount of fly ash and NaOH aqueous solution and the time of the synthesis reaction, the various types of zeolite materials were derived:

**Na-X** (the presence of the phase of Na-X zeolite in the reaction products was determined based on the main d-spacing $d_{001} = 14.47, 3.81, 5.73, 8.85, 4.42, 7.54, 4, 81, and 3.94 \text{ Å})$. The quantitative content of zeolite calculated from X-ray diffraction was 63 %. Microprobe chemical analyses showed that the main exchangeable cation in the zeolite structure is sodium, which balances the net charge of alumino-silicate lattice. Averaged ratios of individual cations obtained by microprobe point analysis EDS were as follows: Na$^+$/Si = 0.55; Na$^+$/K$^+$Ca$^+$/Mg/Si = 0.60; Na$^+$/K$^+$ = 0.65; Na$^+$/K$^+$Ca$^+$/Mg/Si = 0.79; Si/Al = 1.12. Ion exchange capacity of the zeolite material was 18 meq·g$^{-1}$, whereas the surface area was 165 m$^2$·g$^{-1}$. 
Na-P1 (the presence of Na-P1 zeolite phase in the reaction products was determined based on the main d-spacing $d_{hkl} = 7.10, 5.01, 4.10, 3.18 \text{ Å}$). Zeolite content in the reaction products was 81%. Microprobe chemical analyses showed that sodium is the main exchangeable cation in the structure, balancing the charge of the aluminosilicate lattice. Averaged ratios of individual cations derived from the point microprobe chemical analysis EDS were as follows: $\text{Na} + \text{K} + \text{Ca} + \text{Mg}/\text{Si} = 0.44$; $\text{Si}/\text{Al} = 1.42$. The ion-exchange capacity of the derived zeolite material was 0.78 meq·g$^{-1}$, whereas the surface area was 70 m$^2$·g$^{-1}$.

Sodalite (the presence of sodalite phase in the reaction product was determined based on the main d-spacing $d_{hkl} = 6.29, 3.62, 2.09 \text{ Å}$). The quantitative content of the zeolite calculated on the basis of X-ray analysis was 95%. Microprobe chemical analyses showed that sodium is the main exchangeable cation in the structure, balancing the charge of the aluminosilicate network. Averaged ratios of individual cations derived from the point microprobe chemical analysis EDS were as follows: $\text{Na} + \text{K} + \text{Ca} + \text{Mg}/\text{Si} = 1.12$; $\text{Si}/\text{Al} = 1.21$. The ion exchange capacity of sodalite material was 0.56 meq·g$^{-1}$, and the specific surface area was 35 m$^2$·g$^{-1}$.

Na-P1/Linde-A (besides the d-spacing given for the two above-described zeolites in the diffractograms, additionally, d-spacing characteristics for zeolite Linde-A have been identified: 12.31, 8.70, 7.10, 5.50 Å). In total, all three zeolites constituted 63% mass of the products. The presence of zeolite Linde-A and Na-X resulted in the increase of ion exchange capacity, with respect to the Na-P1 material up to 0.73 meq·g$^{-1}$, and surface area to 116 m$^2$·g$^{-1}$, despite the decrease of the zeolite phase content in the reaction product.

Na-P1/Linde-A is quantitatively the total amount of zeolite determined based on X-ray analysis, and it was 64%. The additional presence of zeolite Linde-A resulted in an increase of the ion exchange capacity up to 0.63 meq·g$^{-1}$, and a surface area of 82 m$^2$·g$^{-1}$, despite the decrease of zeolite phases in the reaction product.

### 3.2. Experiments in practical application of the tested zeolite materials in environmental protection

Due to the surface and ion exchange properties of the tested zeolites, they were examined with regard to their application in various fields of environmental engineering. The results of this investigation are shown below.

#### 3.2.1. Removal of ammonium ions

We have tested three synthetic zeolites derived from the hydrothermal reaction of fly ash with NaOH aqueous solution for removal of ammonium ions from aqueous solutions - these materials constituted the following zeolites: Na-X, Na-P1 and synthetic sodalite. Due to the fact that zeolites are good sorbents of ammonium ions in a solution with a low concentration of Na$^+$ (because zeolites are more selective for the capture of Na$^+$ ions than NH$_4^+$ [4, 19]), sorption of these ions was investigated on artificially prepared solutions. Experiment was carried out using ammonium chloride solutions with concentrations in the range of 50-500 mg/dm$^3$.

Studies have shown that the amount of ammonium ions removed from the solution by the tested minerals increases with the increase in the equilibrium concentration in the solution (Fig. 1).

![FIGURE 1 - Sorption curves of NH$_4^+$ for tested zeolite materials.](image-url)
TABLE 2 - The isotherm constants for ammonium exchange by tested zeolite materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>NaX</td>
<td>7.08</td>
<td>0.49</td>
</tr>
<tr>
<td>Na-P1</td>
<td>7.30</td>
<td>0.03</td>
</tr>
<tr>
<td>Sodalite</td>
<td>7.57</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The largest, maximum amount of ammonium ions was adsorbed by the synthetic zeolite Na-X (5 mg NH$_4^+$ g$^{-1}$) at a solution concentration of 400 mg·dm$^{-3}$ of NH$_4$Cl. Slightly lower values were observed for Na-P1 - 4.7 mgNH$_4^+$ g$^{-1}$, and the lowest for sodalite 4.5 mgNH$_4^+$ g$^{-1}$ at a concentration of initial solution of 500 mg·dm$^{-3}$ NH$_4$Cl [17].

From Langmuir and Freundlich sorption isotherms drawn for the analyzed materials, a better fit for Freundlich model is evident, which is obvious in the case of sorption experiments onto solutions. The $R^2$ for this model is very good and in the range of 0.98-0.99 (Table 2).

$K_L$ coefficients for Na-X are much higher than for the other two zeolite materials. However, the coefficient $K_F$ is similar for each sample, which is shown by a better fit of the model. Values of 1/n of all the tested materials are in the range of <1, indicating favorable conditions for the removal of ammonium ions from aqueous solutions [19, 21].

Zeolites such as NH$_4^+$ sorbents were also investigated by Arslan and Veli [43]. They carried out their studies using 4 zeolite samples (Aqua-Multalite, Zeolite of Gordes-Manisa, Zeolite 13X and Zeolite 4A). The results have shown that zeolite 13X provided the highest removal efficiency. The experiments were performed at 23 °C and 150 rpm agitation speed. Optimum conditions were observed at pH 7, zeolite amount of 0.5 g/100 ml, and agitation time of 30 min. The results of the study indicated the best potential for the zeolite 13X as an adsorbent material for ammonium removal.

Zhang et al. [44] used zeolite synthesized from fly ash removal of ammonium from aqueous solutions. The major crystalline structure obtained in the synthesis reaction was identified as faujasite. Using batch experiments, they examined the effects of contact time, pH, initial ammonium concentration, adsorbent dosage, and the presence of other cations and anions. The optimal pH for ammonium removal was found to be 8.0. To obtain the balance between ammonium adsorption capacity and removal efficiency, the optimum adsorbent dosage and initial ammonium concentration were established to be 1.32 g/dm$^3$ and 167.89 mg/dm$^3$, respectively. The authors observed that the presence of individual cations and anions also influenced ammonium removal. The orders were as follows: for cations K$^+>$Ca$^{2+}>Na^+>Mg^{2+}$, and for anions CO$_3^{2-}>Cl^->SO_4^{2-}$, respectively.

3.2.2. Oil refining

The refinery and petrochemical industry has been using the process of adsorption for many years, and this process is now used primarily for the final treatment of light petroleum products, lubricating oils, oils for special use, and paraffins.

It is important for the selection of a sorbent to take into consideration the efficiency of the regeneration process associated with the improvement of oil properties, but also the economic side of the process. In the proper selection of the sorbent, it is necessary to examine some of its properties, especially the refining capacity, selectivity, chemical properties, mechanical strength, costs and facility purchase, and the possibility of reactivation and recycling.

For this purpose, we made laboratory tests of contact refining of used transformer oil (TRAFO collected from ZE Wroclaw) and turbine oil TU-46 taken out from the exploitation onto sorbents prepared based on zeolites (Na-X, Na-P1, sodalite). All zeolite materials were thermally activated for 3 h prior to the refining process at 350 °C, and were crushed in the form of powder before the efficiency of refining was evaluated. The results of this study are summarized in Table 3.

Having analyzed the research results, it can be stated that in the process of refining TRAFO oil by the contact method, zeolite sorbents showed higher efficacy in reducing the acid number for turbine oil (which has a refining effect determined by changes in acid number ranging from 70-79%, and slightly lower efficacy for oil transformer of 41-59%, respectively). The refining effect of turbine and transformer oils achieved by means of zeolite sorbents is comparable to (or slightly higher) than for the commercially available sorbents, such as attapulgite or siliceous earths [35].

TABLE 3 - The influence of the sorbent type on the effect of oil refining.

<table>
<thead>
<tr>
<th>No.</th>
<th>Adsorbent</th>
<th>TRAFO</th>
<th>TU-46</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L_{K_{ref}} = 0.113$; $E_{ref} = 0.449$; $T = 36%$</td>
<td>$L_{K_{ref}} = 0.340$; $E_{ref} = 0.303$; $T = 48%$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>acid number</td>
<td>colour</td>
<td>acid number</td>
</tr>
<tr>
<td>-----</td>
<td>-------------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td>$L_{K_{ref}}$</td>
<td>$W_%$</td>
<td>$E_{ref}$</td>
</tr>
<tr>
<td>1</td>
<td>Na-X</td>
<td>0.062</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>Na-P1</td>
<td>0.046</td>
<td>59</td>
</tr>
<tr>
<td>3</td>
<td>Sodalite</td>
<td>0.066</td>
<td>41</td>
</tr>
</tbody>
</table>
However, the sorbents studied are a bit less effective at removing oil pollution worsening its color (e.g. resin compounds, polymerized compounds) in the case of TRAFO oil (R 48-56%). A significantly lower removal rate was observed for turbine oils, as compared with commercial sorbents, for which the value of refining effect expressed by the bleaching degree was in the range of 8% for the sodalite to 27% for Na-P1, respectively.

Many papers claimed that zeolites have been regarded as one of the most important catalysts in petrochemical industry due to their excellent catalytic performance. However, the micropores predominant in zeolites severely limit their applications in oil refining and natural gas conversion. Therefore, in recent years, mesoporous zeolites have been prepared by introducing mesopores into the zeolite crystals to solve the problem, and thus, they have the advantages of both mesostructured materials (fast diffusion and accessibility for bulky molecules) and microporous zeolite crystals (strong acidity and high hydrothermal stability). Therefore, it is possible to use these mesoporous zeolites as efficient catalysts in oil refining and natural gas conversion including catalytic cracking of heavy oil, alkylation, isomerization, hydrogenation, hydrodesulfurization, methane dehydroaromatization, methanol dehydration to dimethyl ether, methanol to olefins, and methanol to hydrocarbons [45].

Compared with conventional microporous zeolites, the mesoporous zeolites exhibit excellent performance in oil refining and natural gas conversion, such as cracking, hydrogenation and hydrodesulfurization of heavy oil, benzene alkylation, hydroisomerization, methane dehydroaromatization, methanol dehydration to dimethyl ether, methanol to olefins, and methanol to hydrocarbons. These phenomena are reasonably attributed to a fast diffusion and accessibility for reactants and products. However, fluid catalytic cracking is by far the largest user of zeolite catalysts. Recent advances in such catalysts have concentrated on modifying zeolite Y for improved coke selectivity, higher cracking activity, and greater stability through the manipulation of extra framework aluminum, or through the generation of mesoporosity of zeolite crystals. Extra framework aluminum is introduced either by steaming or by ion exchange [45].

3.2.3. Removal of radionuclides from the mine waters

The results of removing both radium isotopes \(^{226}\text{Ra}\) and \(^{228}\text{Ra}\) indicate high efficiency of the process, close to 98%. After passing 120 dm\(^3\) of mine water through the column, \(^{226}\text{Ra}\) concentration decreased to a value of 0.017 kBq m\(^{-3}\), and in the case of isotope \(^{228}\text{Ra}\), to 0.05 kBq m\(^{-3}\). We can conclude that despite the adsorption of about 500 Bq of \(^{226}\text{Ra}\) and about 1000 Bq of \(^{228}\text{Ra}\), no breakthrough of column has occurred. Based on preliminary laboratory tests on "synthetic waters", it was found that for waters with similar concentration of radium ions as in the experiment, a column breakthrough could only occur after passing approximately 1200 dm\(^3\) of water through it, with similar characteristics as in the present experiment [46].

The analysis of the water samples obtained after the process of removing radium ions showed that zeolites have no effect on the levels of calcium or magnesium in purified water; their concentrations after the removal process were about 3000 and 4400 mg dm\(^{-3}\), respectively. Zeolites also do not cause significant changes in the concentration of monovalent metals in the solution. Sodium remains at the level of 50 000 mg dm\(^{-3}\) and potassium of 800 mg dm\(^{-3}\).

The levels of iron, strontium or manganium concentration in the purified water were also, by and large, constant compared to their concentrations before the purification. The zeolite materials tested had no effect on the level of removal of other ions, except for radium. No change in the concentrations of anions (chloride, sulfate or bicarbonate ions) was observed, which are not adsorbed by zeolites due to the negative charge on the surface [46].

The subject of removing radionuclides by means of synthetic zeolite has started to develop. So far, mainly the removal of cesium and strontium were investigated. For example El-Kamash et al. 2006 [47] investigated the possibilities of immobilization of cesium and strontium radionuclides by Type A zeolite-cement blends and lightweight aggregates [48].

The same Type (A) of zeolite was synthesized and evaluated as an inorganic ion exchange material for the removal of Cs and Sr ions from aqueous solutions in both batch and fixed bed column operations. The results showed that the total ion uptake of these metals and the overall bed capacity decreased by increasing the flow-rate, and increased by increasing initial ion concentrations and bed depth. The constants of sorption rate were found to increase with the increase in flow-rate, indicating that the overall system kinetics was dominated by external mass transfer in the initial part of the sorption process in the column [49].

International Atomic Energy Agency [50] carried out tests of the removal of Cs ions for aqueous solutions by synthetic NaA-X zeolite. The zeolite blend was synthesized from fly ash in a 2-step method. Next, the sorption potential of the prepared material for the removal of Cs ions has been evaluated. The results showed that synthetic zeolite blend demonstrates a promising sorption behavior.

However, silver-impregnated zeolites gave promising results in uptake of volatile radioactive iodine and krypton [51]. They achieved best efficiency in comparison with metal-organic framework materials, activated charcoal, or silver-functionalized aerogels. Silver-impregnated zeolites gave iodine decontamination factors as high as 105, iodine loading capacities, and other adsorption parameters including adsorption rates whereas sorbents, including an engineered form of AgZ and selected metal organic framework materials (MOFs), have been successfully demonstrated to capture Kr and Xe.

3.2.4. Removal of zinc ions from the washing baths

Ion exchange is a method used to remove heavy metals from industrial and cooling water and wastes as well. It is
TABLE 4 - Zn(II) ion exchange process parameters on a Na-P1 bed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Na-P1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breakthrough time $\tau_p$, [min]</td>
<td>168</td>
</tr>
<tr>
<td>Time saturation in exchange capacity of the bed $\tau_k$, [min]</td>
<td>279</td>
</tr>
<tr>
<td>The bed volume to the point of breakdown $V_p$</td>
<td>429.0</td>
</tr>
<tr>
<td>The saturation volume in exchange capacity $V_n$</td>
<td>769.0</td>
</tr>
<tr>
<td>Working exchangeable capacity $A_{de}$, [meq·cm$^{-3}$]</td>
<td>0.607</td>
</tr>
<tr>
<td>The maximum exchange capacity $A_{cm}$, [meq·cm$^{-3}$]</td>
<td>1.162</td>
</tr>
</tbody>
</table>

FIGURE 2 - The kinetics of Zn(II) removal under static conditions by the zeolite Na-P1 ($m = 1.30 \pm 0.01$ g, $V = 1$ dm$^3$, $C = 47.85$ mg·dm$^{-3}$).

The data indicated that Na-P1 effectively removes zinc ions from the washing baths.

3.2.4.1 Results of zinc ions removal under dynamic conditions

A flow process of washing baths after galvanizing process was made through a column filled with a zeolite material Na-P1 and sand.

The analysis of the progress and effectiveness of the processes of ion exchange through a Na-P1 bed indicated that the breakthrough of zinc ions took place after 429 bed volumes, and the work time to the point of breakdown was 168 min. After reaching this point, the increase of zinc ion concentration in the effluent took place, while an exhaustion curve strived to achieve the initial concentration of the input solution. Exhaustion of ion exchange properties of Na-P1 bed took place after 769 bed volumes, and the total amount of the removed zinc ions was 1.162 meq·cm$^{-3}$ of the bed (Table 4).

The data indicated that Na-P1 effectively removes zinc ions from the washing baths.

3.2.4.2 Results of zinc ions removal under static conditions

In an experiment conducted in static conditions, the kinetics of ion exchange on Na-P1 zeolite was tested at the natural pH of the mineral, and the acidic pH of added washing baths. The results of the laboratory tests of the contact time impact of Na-P1 and washing baths on the zinc content are shown in Fig. 2.

The results have shown that increasing the shaking time increases the amount of zinc ions removed from the washing baths, until the zinc ion concentration reaches a limit value (2 mg·dm$^{-3}$). Initially, the process is fast because ion exchange probably includes the ions in the crystal lattice of the zeolite minerals that are easily available in interchangeable positions.

In the case of Na-P1, at the initial stage of the process, i.e. after 5 min, the zinc concentration decreased to a value of 2.87 mg·dm$^{-3}$, and decreased gradually. After 30 min of the process of removing zinc, its concentration in the cleaned washings reached 1.26 mg·dm$^{-3}$ i.e. the limit values in wastewaters discharged into water and soil.
The analysis of the results indicated high efficiency of the removal of zinc ions from the washing baths by means of Na-P1. The high efficiency of removal of zinc ions by NaP1 indicated the possibility of wastewater treatment in a batch system.

Zeolites have been widely tested for the removal of heavy metals from various kinds of wastes. Other zeolites produced from fly ash gave very promising results. For example, Wang et al. [52] studied the removal of Cu$^{2+}$ and Zn$^{2+}$ on zeolites A and X from artificially prepared solutions. The results have shown that zeolite A had a higher removal efficiency than zeolite X. For zeolite A, the amount of Cu$^{2+}$ ions adsorbed was 37.99 mg·g$^{-1}$, whereas for Zn$^{2+}$, it was 29.68 mg·g$^{-1}$. For zeolite X, the amount of Cu$^{2+}$ adsorbed was 28.88 mg·g$^{-1}$, whereas for Zn$^{2+}$, it was 22.44 mg·g$^{-1}$, respectively. The observed adsorption behavior was explained by the nature of metals, such as hydrated size, ionic potential and hydrolysis constant and framework structure of zeolites, such as the effective pore size and the amount of exchangeable Na$^+$ bonded to zeolites framework [53, 54].

Bakarat [55] investigated the adsorption capacity of 4A synthetic zeolite for uptake of Cu$^{2+}$, Zn$^{2+}$, Mn$^{2+}$ and Cr$^{4+}$ from aqueous solution. The results have shown that the grain size of the 4A zeolite had a little effect on the adsorption capacity, when the tested zeolite sample was of grain size <90-200 μm. Additionally, the adsorption capacity of the metal ions were found to be strongly dependent on pH. Complete adsorption for Cu$^{2+}$ and Zn$^{2+}$ ions was achieved at pH >6, while the adsorption capacity for both Mn$^{2+}$ and Cr$^{4+}$ was 96% at pH 11 and 55.3% at pH 3, respectively. The optimum contact time was achieved at 1 h, with initial metal ion concentration of 100 mg·L$^{-1}$. For all tested metal ions, the exchange equilibrium was established with a zeolite concentration of 2.5 g·dm$^{-3}$. The removal mechanism of the metal ions was mainly related to the adsorption and ion exchange processes. The experimental data showed a good adjusting of the Langmuir plots which suggests a monolayer coverage of the metal ions on the outer surface of the adsorbent.

3.2.5. Removal of CO$_2$

Greenhouse gas emissions of CO$_2$ are a problem for many industrial plants, such as power plants, cement plants, refineries, etc. That is why there is a need to develop new, cost-effective solutions to reduce carbon dioxide emissions, or neutralize them. Projects in the field of geological CO$_2$ sequestration technology in saline aquifers [56, 57], or in coal seams [58, 59] require continued researches on techniques for capturing carbon dioxide from flue gases.

For CO$_2$ sorption experiments, synthetic zeolite of Na-X type and two zeolite mixtures of Na-P1/Na-X/Linde-A type as well as Na-P1/Linde-A were used [6]. For the sorption experiment, the Na-X zeolite material has been additionally subjected to thermal activation at 350 °C for 4 h.

In order to determine the effect of heat activation on the analyzed material, the surface parameters were defined as follows: ion exchange capacity, the specific surface area as well as structure and pore size distribution.

As a result of the activation of Na-X, the BET surface area after thermal activation increased from 262 to 434 m$^2$·g$^{-1}$. Cation exchange capacity remained almost constant at a level of 218 meq/100 g.

Preliminary sorption of CO$_2$ was conducted for the Na-X zeolite. Isotherm measurements showed significantly improved adsorption on a sample activated; at the equilibrium pressure p/p$_0$ close to 0.01, it reached 0.45 mmol·g$^{-1}$, and on the starting sample 0.18 mmol·g$^{-1}$, which clearly indicates the need of modification of the surface of such a material in order to obtain CO$_2$ sorbents.
In the case of CO₂ sorption (Fig. 4) for other zeolite materials, a mixture of zeolites Na-P1/Na-X/Line-A proved to be the best adsorbent, where the value of adsorption was 0.91 mmol·g⁻¹. The worst results were obtained for the mixture Na-P1/Linde-A (0.39 mmol·g⁻¹) [6].

Regarding other CO₂ separation technologies, membranes also use zeolites. Different types of synthetic zeolites have been used, such as ZSM-5 [60] X and Y types [61, 62], silicalite [63], A type [64], P type [65], ETS-10 [66], mordenite [67], and MCM-41 [68- 71]. CO₂ preferentially permeates CO₂/N₂, CO₂/CH₄ and CO₂/H₂ mixtures but only at low temperatures [70].

However, to get a much better CO₂ adsorption on zeolites, the mesoporous nature of them, as well as the impregnation of amine compounds, or activation by a metal cation substitution i.e. Li⁺, is needed.

CO₂ adsorption capacity of zeolite materials decreases drastically with increased temperature. Additionally, zeolites have very low CO₂ adsorption capacities in the presence of moisture that is present in flue gas, and high uptakes are only obtained under dry conditions [60]. Consequently, the focus for PCC (Post Combustion Capture) has been on solid amines. Solid adsorbent amines have been used successfully for CO₂ adsorption from moist gas at low moderate temperatures. Mesoporous materials are reported to have the highest adsorption capacities of 184 mg·g⁻¹ (4.18 mmol·g⁻¹) at 25 °C for reformulated immobilized amine sorbents and 151 mg·g⁻¹ at 100 °C for tetraethylene-pentamine (TEPA)-loaded SBA-15. Also, polyethyleneimine (PEI)-impregnated MCM-41 at 75 °C has shown CO₂/N₂ selectivity of >1000. Majchrzak-Kučeła et al. [71] have impregnated zeolite MCM-41 with amines such as PEI (poly-ethyleneimine). These tests have shown the improvement of sorption capacity at temperatures typical for flue gases. However, MCM-41 as well SBA-15 are not commercially available yet, and their preparation costs will make their application uneconomical in the near future. Therefore, a continuous search for cheaper CO₂ zeolite adsorbents is required [69].

4. CONCLUSIONS

The research presented in this paper is aimed to demonstrate the wide spectrum of applications of synthetic zeolites derived from fly ash in hydrothermal reaction. The results showed that the zeolite materials maybe well suited for the domain of environmental engineering. The research on the removal of environmental pollutants was carried out only on a laboratory-scale. However, it produced very promising results.

It can be concluded from the experiments in ammonium ion removal that the amount of ammonium ions removed from aqueous solutions increases with the increase in the initial concentration of NH₄⁺ in the purified solution. The removal efficiency of these ions for each of the synthetic zeolites was similar therein. Na-X showed the highest ion exchange capacity in relation to other zeolites tested in this direction (i.e. sodalite, Na-P1).

The tests of oil refining clearly showed that the use of derived synthetic zeolites in this direction is most desirable, and requires this type of application to be continued. These materials showed a similar or higher refining effect than commercially available attapulgite and diatomite, es-
especially for turbine oil where the value of the activity index for each zeolite reached more than 70%. Synthetic zeolites were less efficient when it comes to removing pollution of the color worsening type. Na-P1 was most effective at this experiment, as compared with Na-X and sodalite.

The results of laboratory tests indicate a high application potential of synthetic zeolites for the removal of elevated radionuclides contents in mine water. Various tests have shown high efficiency in the removal of 226Ra and 228Ra which reached 98%. However, the particulate nature of the zeolitic material requires using sand and gravel additive in order to achieve adequate flow-rates through the bed, or a development of a granulation process for the tested zeolites.

The analysis of washings bath purification showed that the Na-P1 sorbents are effective in eliminating the presence of zinc ions from the washings bath. It showed favorable ion exchange process parameters under static and dynamic conditions.

Under static conditions of the washing bath treatment, the recovery time of zinc ions by Na-P1 took 30 min, which indicates that it can be used for the purification of cyclic washings in a reactor (batch type).

In the dynamic conditions, Na-P1, until breakthrough point, purified 429 bed volumes of wastewaters and removed zinc ions of 0.607 meq. Purified washings can be discharged into water and soil, or directed to the process water system.

The experiments conducted have shown that the zeolite materials constitute a competitive material for removal of environmental pollutants, in comparison with commercially available methods/adsorbents. Their additional advantage is the fact that they are produced from waste materials, such as fly ash, which greatly reduces the cost of cleaning technology applied to the contaminants mentioned in the article.

In addition, the use of synthetic zeolites to remove environmental pollutants is confirmed by numerous studies in this area, as it was presented in the section on research results.

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