# RADIOCESIUM ADSORPTION BY ZEOLITIC MATERIALS SYNTHESIZED FROM COAL FLY ASH

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**Abstract:** Brown coal fly ash derived from the combustion of brown-coal in power plant ENO Nováky (Slovak Republic) was used as raw material for synthesis of zeolitic materials ZM1 and ZM3 by hydrothermal alternation with 1M NaOH and 3M NaOH, respectively. Fly ash and synthesized products were characterized using XRF and SEM-EDX analysis. Subsequently, zeolitic materials were tested as sorbents to remove $Cs^+$ ions from aqueous solutions using radiotracer technique. Sorption of cesium by both types of zeolitic materials obeys Langmuir adsorption isotherm model. The maximum sorption capacities $Q_{max}$ at pH 6.0 calculated from Langmuir isotherm were 1203 ± 65 μmol $Cs^+$/ g for ZM1 and 1341 ± 66 μmol $Cs^+$/ g for ZM3. The results showed that alkali treated fly ash can be used as effective sorbent for radiocesium removal from contaminated solutions.

**Key words:** $^{137}Cs$, adsorption, fly ash, hydrothermal zeolitization, zeolitic materials

## 1. Introduction

The development of nuclear science and technology, nuclear weapons testing, generation of electricity in nuclear power plants and the use of radionuclides in a research and medicine have led to the increase production of both liquid and solid wastes containing radionuclides and release of artificial radionuclides into the environment. Radiocesium $^{134}Cs$ and $^{137}Cs$ are one of the most abundant radionuclide in nuclear fission products which has a relatively long half-life and is considered as hazardous element (KHAN, 2003) due to its high solubility what enables easy migration into the environment. Effective separation technologies, e.g. fractional crystallization, solvent extraction, ion exchange using inorganic and organic ion exchangers have been developed for removal of radionuclides from liquid radioactive wastes. The most widely used methods for water treatment to remove radionuclides (Cs, Sr, U, Pu) are those based on co-precipitation and sorption (MILYUTIN *et al.*, 2012). Many researchers have reported about utilization of zeolite and bentonite type minerals for removal of $Cs^+$ ions (YILDIZ *et al.*, 2011; ABD EL-RAHMAN *et al.*, 2006; ATUN and BODUR, 2002). Ion exchange properties of zeolites have been received great attention, especially for application in radioactive liquid waste treatment (ABD EL-RAHMAN *et al.*, 2006; EL-KAMASH *et al.*, 2005). The cationic radioisotopes, present in the liquid effluents of low and intermediate level liquid waste, can be removed by the ion exchange with the $Na^+$ ions of the zeolites. These inorganic materials possess high exchange capacity, selectivity and specificity, good resistant to radiation, and have proven advantages with respect to immobilization and

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final disposal when compared with organic ion exchangers (GONI *et al.*, 2006; LI *et al.*, 2005).

While the particular zeolitic development may take thousands of years in order to form natural zeolites (KOUKOUZAS *et al.*, 2010), formation of synthetic zeolitic materials can be speeded up in the laboratory. In that case the activation solution is an alkaline one, usually NaOH or KOH. The classical alkaline conversion of fly ash (FA) is based on the combination of different [activation solution]/ [fly ash] ratios. The methodologies developed on this field aim at the dissolution of Al-Si bearing phases of the FA and the subsequent precipitation of the zeolitic material (BLISSETT and ROWSON, 2012; AHMARUZZAMAN, 2010; HUI and CHAO, 2006; MOUTSATSOU and PROTONOTARIOS, 2006; QUEROL, 2002; IYER and SCOTT, 2001; HOLLMAN, 1999; AMRHEIN *et al.*, 1996; SHIGEMOTO *et al.*, 1993).

In addition, the application of fly ash can contribute to the solution of another environmental problem, namely accumulation of fly ash produced by burning of coal in power stations. Fly ash is a massing waste material containing hazardous substances which may be released to the environment from dumping places which are still enlarged. In spite of the fact that there exist many ways of utilization of this toxic pollutant (e.g. civil engineering, metallurgy, mining, agriculture, etc.) it is necessary to increase the amount of fly ash being re-utilized. Single fly ash is known for low sorption capacities. However, after its alternation, products with better ion-exchange properties and several fold-enlarged surfaces comparable with natural zeolites can be obtained. Of the many applications of fly ash, zeolite synthesis has been reported to be of great interest due to the fact that zeolites have wide industrial application (MUSYOKA *et al.*, 2013).

In our work the brown coal fly ash was utilized for synthesis of two types of zeolitic materials. The main motivation for this work was inspired by the need for effective sorbents for radiocesium that are essential for purifying the radioactive contaminated aqueous solutions. The key objectives of our research are as follows: (a) to characterize fly ash and products of its hydrothermal alternation using scanning electron microscopy connected with EDX and X-ray fluorescence analysis; (b) to quantify sorption capacity of fly ash and zeolitic materials, and (c) to investigate the major mechanisms of cesium ions sorption. Equilibrium isotherm models according to Langmuir and Freundlich were used for mathematical description of sorption equilibrium in single systems. To obtain reliable experimental sorption data within a broad concentration range, radiotracer technique with $^{137}$CsCl was used.

## 2. Material and methods

### 2.1 Sorbent preparation

Brown-coal fly ash (density $\rho$ = 2 850 kg/m$^3$) was obtained from power station Nováky (ENO) (Zemianske Kostoľany, Slovak Republic) and was stored in sealed containers before use. Fluid fly ash was washed in deionised water (0.054 µS/cm Simplicity 185, Millipore, USA) and oven-dried for 24 h at 60°C. Dried ash was used as the raw material for zeolite synthesis according to the method of QUEROL *et al.* (2001). Fly ash (100 g) was resuspended in 300 ml of 1.0 M or 3.0 M NaOH for ZM1 and ZM3 preparation, and the mixture was boiled under reflux for 18 h. The products of hydrothermal zeolitization were thoroughly washed 3 times in surplus of deionised water, oven-dried for 24 h at 60°C and were stored in sealed containers before use in sorption experiments.

## 2.2 Sorbent characterization

The surface structure analysis of sorbents (fly ash, ZM1 and ZM3) before and after $Cs^+$ sorption and EDX microanalysis were performed by scanning electron microscope VEGA 2 SEM (TESCAN Inc., Czech Republic) coupled with QUANTAX QX2 detector (RONTEC, Germany) for electron dispersive X-ray analysis. Prior to the SEM and EDX analysis, the samples were dried for 24 h at 80°C and stuck to a sample holder using conductive adhesive (Ag). Samples were then coated with Au using BP 343.7 Evaporator (TESLA ELMI Inc., Czech Republic). The analyses were performed at voltage 30 kV and vacuum pressure $9.0\times10^{-3}$ Pa. Elemental analysis of fly ash and zeolitic materials was performed by X-ray fluorescence analysis using high performance X-ray fluorescence spectrometer X-LAB 2000, SPECTRO, Germany. For determination of specific surface area (SSA) zeolitic material was subjected to $N_2$ adsorption using BET method (BRUNAUER *et al.*, 1938).

## 2.3 Adsorption experiments

Batch adsorption experiments were carried out by suspending the sorbent (2.5 g/dm$^3$, d.w. of fly ash, zeolitic material ZM1 and ZM3) in solutions with concentrations of 4000 μmol/dm$^3$ of CsCl (analytical grade, Sigma Aldrich, Germany) spiked with $^{137}$Cs at pH adjusted to 6.0. The content was agitated on reciprocal shaker (120 rpm) at 22 °C. In time periods (5, 30, 60, 120, 240, 360 and 1440 min.) aliquot samples of solution were taken from individual flasks for radiometric determination of $^{137}$Cs. The $Cs^+$ uptake was calculated as:

$$Q_{eq} = (C_0 - C_{eq})\frac{V}{M} \quad (1)$$

where $Q$ is the uptake (μmol/g), $C_0$ and $C_{eq}$ are the initial and the final $Cs^+$ concentrations in solution (μmol/dm$^3$), $V$ is volume (dm$^3$) and $M$ is the amount of dried sorbent (given in grams).

For determination of the adsorption capacity of sorbents batch equilibrium experiments were carried out in solutions of CsCl in concentration range 100-6000 μmol/dm$^3$, spiked with $^{137}$Cs. pH was adjusted to 6.0. The content was agitated on a reciprocal shaker (120 rpm) for 6 h at 22°C. To evaluate the effect of the pH on the uptake of Cs by studied sorbents, experiments were carried out in CsCl solutions (4000 μmol/dm$^3$) spiked with $^{137}$Cs at pH ranging from 2.0 to 8.0. The content was agitated on reciprocal shaker (120 rpm) for 6 h at 22 °C. At the end of the experiments the sorbent was filtered out, washed in deionized water and the radioactivity of both the sorbent and the liquid phase was measured.

## 2.4 Radiometric analysis

The gamma spectrometric assembly using the well type scintillation detector 54BP54/2-X, NaI(Tl) (Scionix, the Netherlands) and the data processing software Scintivision 32 (ORTEC, USA) were used for obtaining quantitative data of $Cs^+$ sorption by sorbents at the energy of $\gamma$ – photons: $^{137}Cs$ – 661.64 keV. Standardized $^{137}CsCl$ solution (5.4 MBq/cm$^3$, CsCl 20 mg/dm$^3$ in 3 g/dm$^3$ HCl) was obtained from the Czech Institute of Metrology, Prague (Czech Republic).

## 2.5 Data analysis

The Langmuir (Eq. 2) and Freundlich (Eq. 3) adsorption models were used for describing equilibrium data. The integral equations are as follows:

$$Q_{eq} = \frac{bQ_{\max}C_{eq}}{1 + bC_{eq}} \tag{2}$$

$$Q_{eq} = KC_{eq}^{(1/n)} \tag{3}$$

where $Q_{max}$ represents the maximum sorption capacity upon complete saturation of the sorbent, $b$ is a constant related to the energy of adsorption. $K$ and $1/n$ values are the Freundlich constants referring to adsorption capacity and intensity of adsorption, respectively. The $Q_{max}$ values and the corresponding parameters of adsorption isotherms were calculated using the non-linear regression analysis performed by ORIGIN 7.0 Professional (OriginLab Corporation, Northampton, USA). The theoretical Cs speciation in solution was calculated using MINEQL+ Chemical Equilibrium Modeling System (version 4.6 for Windows).

# 3. Results and discussion

## 3.1 Synthesis of zeolitic materials and their characterization

The chemical composition of zeolitic material ZM1 and ZM3 prepared from brown coal fly ash by hydrothermal activation is given in Table 1. The main components of fly ash are $SiO_2$ (54.7%) and $Al_2O_3$ (19.2%) which present elementary building blocks for preparation of synthetized zeolites. Concentration of these components was further decreased in both zeolitic materials ($SiO_2$ from 54.7 to 50.1% (ZM1) and 42.2% (ZM3)) as a result of dissolution within zeolitization in NaOH. Moreover, during the hydrothermal activation, both alumina and silicate ions are condensed and formed aluminum–silicate gel. Evident increase in $Na_2O$ amount from 1.0 (coal fly ash) to 6.2% (ZM1) and 9.8% (ZM3) is due to entrapment of sodium ions to neutralize the negative charge on aluminosilicate gel (Table 1). NaOH causes differentiation in the distribution of the electric charge between the Al-O and Si-O bonds and the enhancement of the chemically active centres in the lattice. As was mentioned by other authors (KOUKOUZAS *et al.*, 2010) generation of terminal groups such as ≡Si-OH, ≡Si-ONa, ≡Si-O-, $(\equiv\text{Si-O})_3$Al-O- in the presence of NaOH lead to the formation of zeolitic materials.

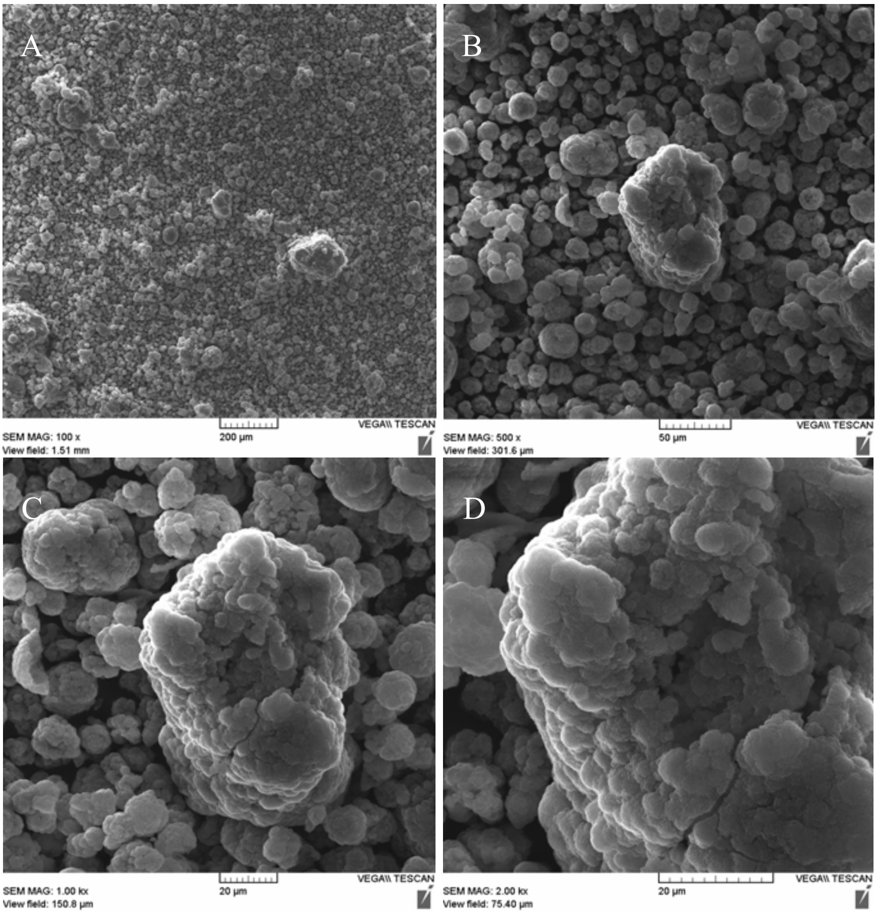

Fig. 1. Scanning electron micrographs of zeolitic material ZM3 – magnification: (A) 100×; (B) 500×; (C) 1000× and (D) 2000×.

The SEM microscopy was used for surface characterization of raw fly ash and synthesized ZM1 and ZM3. Although the synthesized zeolitic materials keep the original spherical shape of raw fly ash, pseudomorphs (zeolitic aggregates) on the surface of fly ash particles were created (Fig. 1A-D). Similar formation of pseudomorphs after hydrothermal reaction was observed by RÍOS *et al.* (2009). MURAYAMA *et al.* (2002) have synthetized zeolites in solutions of $Na_2CO_3$ and/or KOH. They observed that the crystal of zeolite P synthesized in $Na_2CO_3$ solution covers like a thin film on the fly ash surface. On the other hand, in the case of KOH solution, chabazite crystal grows as an ellipsoid on the fly ash surface.

Table 1. The chemical composition of brown coal fly ash and synthesized zeolitic materials ZM1 and ZM3 (wt. %).

| Component (%) | **$SiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **CaO** | **MgO** | **MnO** | **$TiO_2$** | **$K_2O$** | **$Na_2O$** | **$P_2O_5$** | **$SO_3$** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw fly ash | 54.7 | 19.2 | 9.88 | 5.39 | 2.07 | 0.09 | 0.73 | 2.30 | 1.00 | 0.19 | 0.58 |
| ZM1 | 50.1 | 18.8 | 8.38 | 4.16 | 2.10 | 0.09 | 0.61 | 2.06 | 6.20 | 0.13 | 0.09 |
| ZM3 | 42.2 | 18.9 | 8.94 | 5.85 | 2.25 | 0.10 | 0.67 | 1.63 | 9.80 | 0.06 | 0.08 |

## *3.2 Influence of pH on cesium adsorption*

The pH value presents one of the crucial parameters in the sorption of radionuclides heavy metals by zeolites and zeolitic materials. Aqueous liquid radioactive waste is generated during nuclear reactor operations and during industrial and institutional application of radioisotopes. The chemical compositions and radioactivity levels of the generated wastes depend on the conducted operation (ABDEL-RAHMAN *et al.*, 2011). Also the pH of aqueous radioactive waste depends on its origin. Therefore, to investigate the influence of pH on sorption of $Cs^+$ ions, experiments were conducted in the pH range from 2.0 to 8.0.

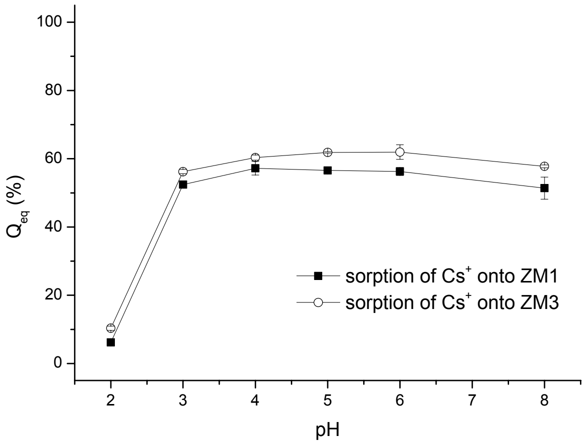

Fig. 2. Effect of initial pH on sorption of $Cs^+$ ($C_0$ = 4000 μmol/dm$^3$ CsCl, 60 kBq/dm$^3$ $^{137}Cs$) by zeolitic material ZM1 and ZM3 ($C_S$ = 2.5 g/dm$^3$, d.w.) from single metal solution. Error bars represent standard deviation (SD) of the mean (*n = 2*).

The effect of initial pH on Cs sorption is depicted in Fig. 2. It was observed that cesium ions´ binding is pH dependent and that the amount of sorbed metal ions increased with increasing pH of the solution. Increasing pH value causes that the netelectronegativity of zeolitic materials increases as a result of deprotonation of active sites present on surface. The highest uptake was observed at pH ranging from 5.0 to 6.0 and reached 57% (ZM1) and 61% (ZM3) respectively.

Observed negligible sorption at pH 2.0 is closely related to competition between $H^+$ and $Cs^+$ ions for occupancy of the active sites. The slight decrease of Cs sorption at pH 8.0 is attributed to the abundance of $OH^-$ that results in an increased hindrance to the diffusion of cesium ions. RAO *et al.* (2006) pointed out that mineral acids affect the structure of zeolites In the zeolite framework, the Si-O-Al is weaker than Si-O-Si and can easily be attached by $H^+$ ions affecting the zeolite structure. This defect is more pronounced in the case of zeolites with low Si/Al ratios such as zeolite A and X (RAO *et al.*, 2006), as well as studied zeolitic materials ZM1 and ZM3. The extent of the damage to their structure depends on the pH of the solution. The structure of zeolites with low Si/Al ratios may collapse in the presence of acids with pH lower than 5.0, but the severity would be more below pH value of 3.0 (EL-KAMASH, 2008). Aluminosilicate structure is vulnerable also to strong basic environments since strong bases can lead to desilication (MISHRA and TIWARI, 2006). These morphological changes could influence the ZM sorption capacity.

The pH of the solution also influences the ionization and speciation of metals in aqueous solutions. Metals can form various ionic forms depending on the pH of solution. It is generally known that zeolites have a very little affinity to anionic complexes due to their negative framework structure (ZIYATH *et al.*, 2011). According to speciation calculation (Visual MINTEQ ver. 3.0) cesium, in pH from 2.0 to 8.0, exists exclusively in two forms $Cs^+$ (>99.9%) and CsCl (0.1%) indicating that speciation has no significant influence on cesium uptake by zeolitic materials. Due mentioned facts, all further experiments in present study were carried out at initial pH value of 6.0.

## *3.3 $Cs^+$ sorption kinetics by zeolitic materials and fly ash*

Zeolitic materials (ZM1 and ZM3) prepared from coal fly ash represent well sedimenting material with a large specific surface area, suitable for sorption of dissolved solutes primarily metal ions and radionuclides. The kinetic studies on the adsorption of cesium ions from single system by zeolitic materials and brown coal fly ash were performed to determine the minimum time needed to reach the sorption equilibrium. Results showed that the Cs sorption by zeolitic materials is a rapid process (Fig. 2). Maximum uptake, 933 μmol/g (59%) in case of ZM1 and 1015 μmol/g (63%) in case of ZM3 at sorbent dosage 2.5 g/$dm^3$, initial cesium concentration $C_0$ = 4000 μmol/$dm^3$ and 22 °C, was recorded after 30 min and equilibrium was established within 60 min. After this time there was no significant increase during next 23 hours, although a slight decrease of Cs uptake in case of ZM1 was observed. At the initial phase, rapid uptake of cesium ions onto surface of zeolitic materials occurs. Subsequently, the $Cs^+$ ions diffused into the crystal structure through the micropores followed by chemical and physical adsorption at the active sites of the pores. Contrary, the equilibrium sorption of $Cs^+$ ions by raw fly ash was obtained after 60 min and the cesium uptake reached only 4 μmol/g, indicating negligible affinity of fly ash towards cesium ions. EL-NAGGAR *et al.* (2008) also observed very fast sorption of cesium ions by NaA-X zeolite blend from fly ash. The largest amount of cesium ions was adsorbed within the first 90 min. Maximum sorption of $Cs^+$ ions by Turkish clays (bentonite, zeolite, sepiolite and kaolinite) was reached within 4h (BAYÜLKEN *et al.*, 2010). Similarly, the kinetic studies of FAGHIHIAN *et al.* (2013) showed that the process of $Cs^+$ and $Sr^{2+}$ sorption onto magnetic zeolite nanocomposite was quite rapid and 90% of equilibrium capacity was achieved within 30 min. On the contrary, YILDIZ *et al.* (2011), who studied the sorption behavior of $Cs^+$ ions on clay minerals and zeolite from radioactive waste, found that in all cases, equilibrium was reached in about 2 days.

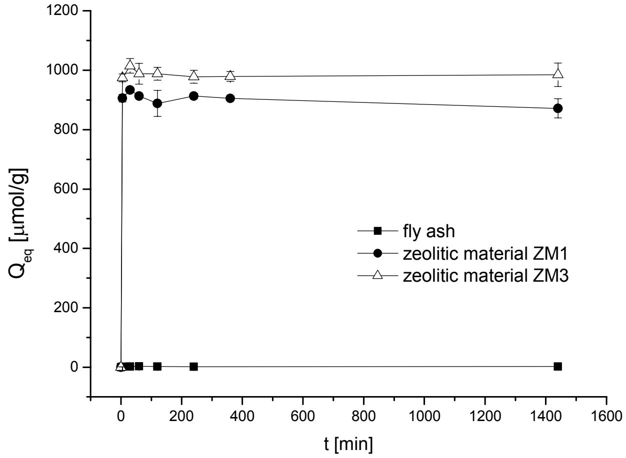

Fig. 2. Sorption kinetics of $Cs^+$ ions by coal fly ash ($C_0$ = 1000 μmol/dm$^3$ CsCl, 60 kBq/dm$^3$ $^{137}Cs$, $C_S$ = 2.5 g/dm$^3$, d.w.) and zeolitic materials ZM1, ZM3 ($C_0$ = 4000 μmol/dm$^3$ CsCl, 60 kBq/dm$^3$ $^{137}Cs$, $C_S$ = 2.5 g/dm$^3$, d.w.) at 22°C and pH 6.0.

## *3.4 Sorption isotherm study*

The cesium sorption equilibrium is shown in Fig. 3. On the basis of obtained results we found that sorption capacity for cesium was 287 times higher (ZM1) and 316 times higher (ZM3) in comparison with raw coal fly ash. Due to the fact that we observed only negligible sorption capacity for cesium in case of fly ash, this sorbent was not used in further experiments.

The Langmuir (Eq. 2) and Freundlich (Eq. 3) isotherms were fitted to the equilibrium data for $Cs^+$ sorption on ZM1 and ZM3. Parameters of the models determined from the experimental data using non-linear regression analysis are reported in Table 2. In both cases the Langmuir isotherm fits experimental data better than the Freundlich isotherm, as is demonstrated by the more homogeneous standard deviation of each observed parameter obtained and by the Akaike´s information criterion values (Table 2).The maximum sorption capacity $Q_{max}$ of zeolitic materials for cesium obtained from Langmuir isotherm was 1203 ± 65 μmol/g for ZM1 and 1341 ±

66 µmol/g for ZM3, indicating slightly higher sorption capacity of ZM3 for cesium cations. Affinity constant *b* indicate similar affinity of both materials for $Cs^+$ ions at low concentrations (ZM1 $b = 0.0042$; ZM3 $b = 0.0036$). The difference in $Q_{max}$ values is related to reaction conditions of zeolite preparation. For preparation of zeolitic material ZM3, by hydrothermal synthesis of fly ash, higher NaOH concentration (3 M) was used. This fact relates with higher molar content of exchangeable $Na^+$ ions in the final product in comparison with ZM1 and raw coal fly ash (Table 1). The difference in maximum sorption capacities of studied materials was more visible in case of $Cd^{2+}$ ions sorption. The $Q_{max}$ were 696 ± 22 µmol/g for ZM1 and 1160 ± 44 µmol/g for ZM3 indicating higher capacity of ZM3 for cadmium (REMENÁROVÁ *et al.*, 2014).

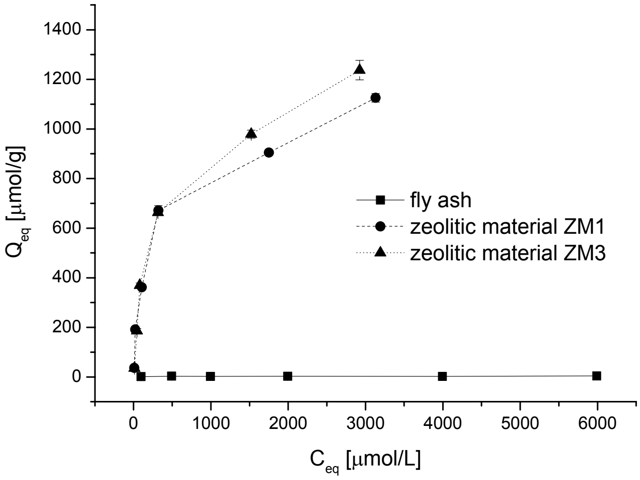

Fig. 3. The equilibrium sorption of $Cs^+$ ions onto: (-■-) fly ash, (-●-) zeolitic material ZM1 and (-▲-) zeolitic material ZM3 (2.5 g/dm$^3$, d.w.) after 6 h at 22°C, initial pH 6.0.

Table 2. Langmuir and Freundlich isotherm model parameters (± SD) for sorption of $Cs^+$ ions onto zeolitic material ZM1 and ZM3 at pH 6.0 (6 h, 22 °C) calculated using non-linear regression analysis.

| **Isotherm model** | $Q_{max}$ **[µmol/g]** | ***b*** **[dm$^3$/µmol]** | ***K*** **[dm$^3$/g]** | **1/*n*** | $R^2$ | **Akaike´s weight** |
|---|---|---|---|---|---|---|
| Zeolitic material ZM1 | | | | | | |
| Langmuir | 1203 ± 65 | 0.0042 ± 0.0008 | - | - | 0.989 | 97.58 |
| Freundlich | - | - | 76.4 ± 31.4 | 0.34 ± 0.06 | 0.951 | 2.42 |
| Zeolitic material ZM3 | | | | | | |
| Langmuir | 1341 ± 66 | 0.0036 ± 0.0006 | - | - | 0.992 | 97.93 |
| Freundlich | - | - | 62.9 ± 26.1 | 0.37 ± 0.06 | 0.960 | 2.07 |

It can be seen from Table 2 that the Freundlich intensity constant *n* are greater than unity for both studied zeolitic materials. This has physicochemical significance with reference to the qualitative characteristics of the isotherms, as well as to the interactions between metal ions species and zeolite (EL-KAMASH, 2008). Value $n > 1$ indicates that the zeolitic material has an increasing tendency for sorption with increasing sorbent concentration. This should be attributed to the fact that with progressive surface coverage of adsorbent, the attractive forces between the metal ion species such as van der Waals forces, increases more rapidly than the repulsive forces, exemplified by short-range electronic of long-range Coulombic dipole repulsion, and consequently, the metal ions manifest a stronger tendency to bind to the zeolitic materials (ABD EL-RAHMAN *et al.*, 2006; MOHAN and SINGH, 2002).

Table 3 compares the maximum sorption capacities $Q_{max}$ of various inorganic sorbents for removing of cesium cations. Comparison of $Q_{max}$ values obtained in our work with those of other authors indicates that studied synthetic zeolitic materials prepared from coal fly ash belong to the group of sorbents with significantly higher sorption capacity for cesium.

Table 3. Comparison of $Q_{max}$ values of different inorganic sorbents for $Cs^+$ ions.

| Sorbent | $Q_{max}$ [μmol/g] | References |
|---|---|---|
| magnetic zeolite | 1725 | FAGHIHIAN *et al.* (2013) |
| zeolite A | 1561 | EL-KAMASH (2008) |
| bentonite J15 | 850 | GALAMBOŠ *et al.* (2010) |
| bentonite K15 | 950 | GALAMBOŠ *et al.* (2010) |
| bentonite L15 | 550 | GALAMBOŠ *et al.* (2010) |
| montmorillonite K10 | 280 | GALAMBOŠ *et al.* (2010) |
| zeolite (fine) | 1610 | BAYÜLKEN *et al.* (2010) |
| zeolite (coarse) | 671 | BAYÜLKEN *et al.* (2010) |
| coal fly ash | 4* | present study |
| zeolite ZM1 | 1203 | present study |
| zeolite ZM3 | 1341 | present study |

* maximum sorption capacity $Q_{max}$ determined experimentally

## 3.5 Sorption mechanism

Due to the fact that obtained results indicate higher capacity of ZM3 for cesium ions, sorption mechanism will be discussed only for ZM3. The specific surface area was determined from the $N_2$ adsorption isotherm by applying the Brunauer-Emmett-Teller equation (BRUNAUER *et al.*, 1938). The specific surface area (SSA) of ZM3 evaluated from BET isotherm equals to 9.24 $m^2/g$. In the literature is often found an inconsistence in determination of specific surface area of zeolites and zeolitic materials. Significantly higher values of SSA were obtained in case of cancrinite-type zeolite synthetized from fly ash (278.9 $m^2/g$) produced by QIU and ZHENG (2009), NaA-X zeolite blend from fly ash (593.6 $m^2/g$) (EL-NAGGAR *et al.*, 2008) and ZFA (278.9 $m^2/g$) (QIU and ZHENG, 2009). This inconsistency could be associated with differences in the properties of zeolites, their origin and the method of study (CHOJNACKI *et al.*, 2004). In case of synthetized zeolites, the differences in SSA are also related with the original fired coal, type of used combustion technology and also the type of used additives (e.g., for stabilization of flame). WANG *et al.* (2009) reported that the removal of heavy metals increased with the increase in the specific surface area of zeolite. However, some studies have reported that the increase in specific surface area does not necessarily increase the sorption capacity (OREN & KAYA, 2006; LEYVA-RAMOS *et al.*, 2004). SSA value of ZM3 was rather low indicating that the material either has low sorption capacity or the dominating mechanism of sorption is different than physical adsorption. Maximum sorption capacity acquired rather high values indicating that the physical adsorption is not the main binding mechanism.

Table 4. Predicted values of $pK_a$ constants and site concentration of functional groups on zeolitic material ZM3. Potentiometric titration of ZM3 (3 g/dm$^3$) was performed by 0.1 M NaOH in 0.1 M NaCl at 25 °C. Calculated by ProtoFit ver. 2.1 software.

| **Functional group** | $pK_a$ | $c_{An}$ **[mmol/g]** | ***pHzpc*** |
|---|---|---|---|
| 1 | 0.00 – 1.46 | $0.020 \times 10^{-3}$ | 10.9 |
| 2 | 5.76 – 5.95 | 0.013 | |
| 3 | 9.55 – 10.60 | 1.050 | |
| 4 | 11.10 – 11.20 | 1.910 | |
| | | ∑ 2.97302 | |

On the basis of the chemical nature of zeolites, most studies (REMENÁROVÁ *et al.*, 2014; MERRIKHPOUR and JALALI, 2013; QIU and ZHENG, 2009; SPRYNSKYY *et al.*, 2006; ERDEM *et al.*, 2004) expect that the dominating mechanism of metal cations sorption is ion-exchange in which cations in the zeolite framework are replaced by metal cations present in water.

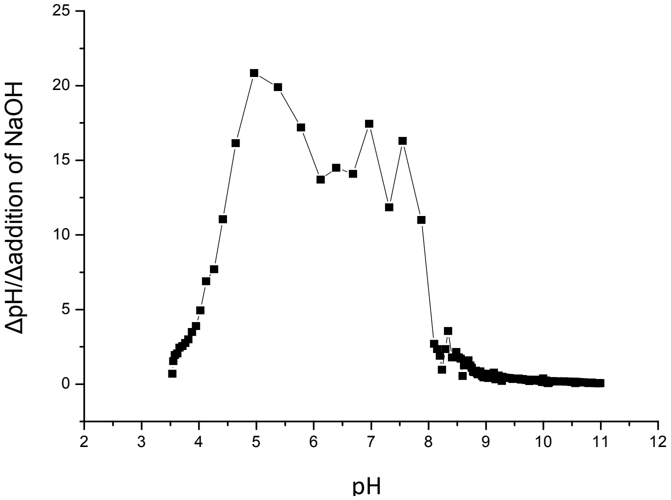

Fig. 4. Potentiometric titration of zeolitic material ZM3 prepared from coal fly ash (3.0 g/dm$^3$) expressed in the form of first derivation according to Gran. Titration performed with 0.1 M NaOH at background electrolyte 0.1 M NaCl and 25 °C.

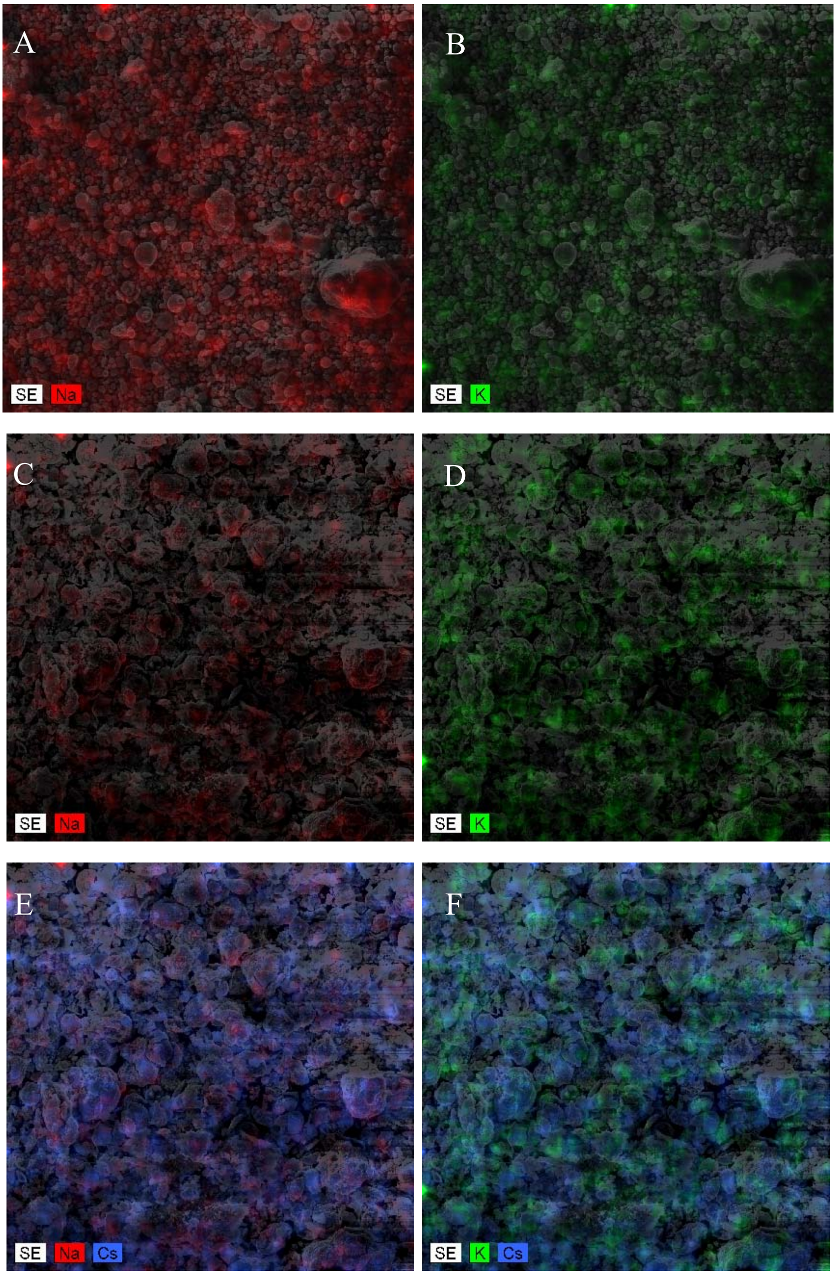

Fig. 5. Scanning electron micrographs of zeolite ZM3: (A,B) before and (C-F) after cesium sorption (6000 µmol/dm$^3$ CsCl) at pH 6.0; magnification 150. EDX elemental mapping of Na and K on zeolite ZM3: (A, B) before and (C, D) after cesium sorption; and (E, F) elemental mapping of Na, K and Cs after cesium sorption.

To identify the types and the amount of functional groups present on the ZM3 surface, potentiometric titration of ZM3 was performed. For calculation of $pK_a$ values of functional groups and corresponding site concentrations $c_{An}$ from titration curve behavior the modeling software ProtoFit using the non-electrostatic model (NEM) was used (Table 4). It was found that a four-site model provided a good fit of titration data and the results revealed the presence of four functional groups. Their detailed chemical identification was not possible. Fig. 4 illustrates potentiometric titration curve of ZM3. Total ion exchange capacity of zeolitic material ZM3 was 2.97 mmol/g, giving the theoretical maximum sorption capacity of ZM3 for Cs ions 2970 µmol/g.

In previous experiments (REMENÁROVÁ *et al*., 2014) we confirmed by SEM EDX analysis and elemental mapping that the main mechanism of $Cd^{2+}$ ions binding onto zeolitic materials was ion-exchange. Similar results were obtained also in case of Cs sorption. Evident decrease of sodium and also potassium and calcium peaks after Cs sorption was observed on the EDX spectra indicating the key role of ion-exchange mechanism on $Cs^+$ ions sorption by zeolitic materials (data not shown). The expected replacement of sodium and potassium ions by cesium is evident from Fig. 5A-F. It has to be pointed out that beside ion-exchange also other mechanisms such as physisorption and chemisorption partly participate on Cs binding by zeolitic materials. This statement was also confirmed by slight decrease of sorption capacity at pH 8.0 which cannot be interpreted with a pure ion-exchange mechanism because pH-dependent surface sites would be expected to retain more cesium as the pH was elevated (BAYÜLKEN *et al*., 2010).

## 4. Conclusions

Zeolitic materials based on brown coal fly ash produced by power plant ENO Nováky (Slovak Republic) were successfully synthesized by hydrothermal alternation. The results showed that zeolitic materials present excellent adsorbents for the removal of cesium ions from liquid radioactive wastes. Sorption capacities of studied zeolitic materials for $Cs^+$ ions removal are more than 287 times higher in case of ZM1 and more than 316 times higher in case of ZM3 compared with the sorption capacity of the original coal fly ash. Zeolitic materials demonstrate high sorption capacities and rapid uptake of cesium ions from aqueous solutions. The values of $Q_{max}$ calculated from Langmuir isotherm ($Q_{max}$) were 1203 ± 65 µmol/g for ZM1 and 1341 ± 66 µmol/g for ZM3 indicating slightly higher capacity of ZM3 for cesium. SEM-EDX analysis confirmed surface retention of cesium and the participation of ion-exchange mechanism. Reported results indicate that synthesized zeolitic materials could be suitable as sorbents for removal of radiocesium from liquid radioactive wastes.

## References

ABD EL-RAHMAN, K.M., EL-KAMASH, A.M., EL-SOUROUGY, M.R., ABDEL-MONIEM, N.M.: Thermodynamic modeling for the removal of $Cs^+$, $Sr^{2+}$, $Ca^{2+}$, and $Mg^{2+}$ ions from aqueous waste solutions using zeolite A. J. Radioanal. Nucl. Chem., 268, 2006, 221-230.

ABDEL-RAHMAN, R.O., IBRAHIUM, H.A., HUNG, Y.-T.: Liquid radioactive wastes treatment: a review. Water, 3, 2011, 551-565.

AHMARUZZAMAN, M.: A review on the utilization of fly ash. Prog. Energy Combust. Sci., 36, 2010, 327–363.

AMRHEIN, C., HAGHNIA, G.H., KIM, T.S., MOSHER, P.A., GAGAJENA, R.C., AMANIOS, T., DE LA TORRE, L.: Synthesis and properties of zeolites from coal fly ash. Environ. Sci. Technol., 30, 1996, 735–742.

ATUN, G., BODUR, N.: Retention of Cs on zeolite, bentonite and their mixtures. J. Radioanal. Nucl. Chem., 253, 2002, 275-279.

BAYÜLKEN, S., BAŞÇETIN, E., GÜÇLÜ, K., APAK, R.: Investigation and modeling of cesium(I) adsorption by Turkish clays: bentonite, zeolite, sepiolite, and kaolinite. Environ. Prog. Sustain. Energy, 30, 2010, 70-80.

BLISSETT, R.S., ROWSON, N.A.: A review of the multi-component utilisation of coal fly ash. Fuel, 97, 2012, 1–23.

CHOJNACKI, A., CHOJNACKA, K., HOFFMAN, J., GÓRECKI, H.: The application of natural zeolites for mercury removal: from laboratory tests to industrial scale. Miner. Eng., 17, 2004, 933-937.

EL-KAMASH, A.M., ZAKI, A.A., ABD ELGELEEL, M.: Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A. J. Hazard. Mater., 127, 2005, 211-220.

EL-KAMASH, A.M.: Evaluation of zeolite A for the sorptive removal of $Cs^+$ and $Sr^{2+}$ ions from aqueous solutions using batch and fixed bed column operations. J. Hazard. Mater., 151, 2008, 432-445.

EL-NAGGAR, M.R., EL-KAMASH, A.M., EL-DESSOUKY, M.I., GHONAIM, A.K.: Two-step method for preparation of NaA-X zeolite bled from fly ash for removal of cesium ions. J. Hazard. Mater., 154, 2008, 963-972.

ERDEM, E., KARAPINAR, N., DONAT, R.: The removal of heavy metal cations by natural zeolites. J. Colloid Interface Sci., 280, 2004, 309-314.

FAGHIHIAN, H., MOAYED, M., FIROOZ, A., IRAVANI, M.: Synthesis of a novel magnetic zeolite nanocomposite for removal of $Cs^+$ and $Sr^{2+}$ from aqueous solution: kinetic, equilibrium and thermodynamic studies. J. Coll. Int. Sci., 393, 2013, 445-451.

GALAMBOŠ, M., PAUČOVÁ, V., KUFČÁKOVÁ, J., ROSSKOPFOVÁ, O., RAJEC, P., ADAMCOVÁ, R.: Cesium sorption on bentonites and montmorillonite K10. J. Radioanal. Nucl. Chem., 284, 2010, 55-64.

GONI, S., GUERRERO, A., LORENZO, M.P.: Efficiency of fly ash belite cement and zeolite matrices for immobilizing cesium. J. Hazard. Mater., B137, 2006, 1608-1617.

HOLLMAN, G.: A two step process for the synthesis of zeolites from coal fly ash. Fuel, 78, 1999, 1225–1230.

HUI, K., CHAO, C.: Pure, single phase, high crystalline, chamfered-edge zeolite 4A synthesized from coal fly ash for use as a builder in detergents. J. Hazard. Mater. 137, 2006, 401–409.

IYER, R., SCOTT, J.: Power station fly ash — a review of value-added utilization outside of the construction industry. Resour. Conserv. Recycl., 31, 2001, 217–228.

KHAN, S.A.: Sorption of the long-lived radionuclides cesium-134, strontium-85 and cobalt-60 on bentonite. J. Radioanal. Nucl. Chem., 258, 2003, 3-6.

KOUKOUZAS, N., VASILATOS, C., ITSKOS, G., MITSIS, I., MOUTSATSOU, A.: Removal of heavy metals from wastewater using CFB-coal fly ash zeolitic materials. J. Hazard. Mater., 173, 2010, 581-588.

LEYVA-RAMOS, R., AGUILAR-ARMENTA, G. GONZALEZ-GUTIERREZ, L.V., GUERRERO-CORONADO, R.M., MENDOZA-BARRON, J.: Ammonia exchange on clinoptilolite from mineral deposits located in Mexico. J. Chem. Tech. Biotechnol., 79, 2004, 651-657.

LI, J., GONG, Z.W., JIANLONG, W.: Solidification of low-level radioactive resins in ASC zeolite blends. Nucl. Eng. Design, 235, 2005, 817-821.

MERRIKHPOUR, H., JALALI, M.: Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite. Clean Technol. Environ. Policy, 15, 2013, 303-316.

MILYUTIN, V.V., GELIS, V.M., NEKRASOVA, N.A., KONONENKO, O.A., VEZENTSEV, A.I., VOLOVICHEVA, N.A., KOROĽKOVA, S.V.: Sorption of Cs, Sr, U, and Pu radionuclides on natural and modified clays. Radiochemistry, 54, 2012, 75-78.

MISHRA, T., TIWARI, S.K.: Studies on sorption properties of zeolite derived from Indian fly ash. J Hazard Mater, 137, 2006, 299-303.

MOHAN, D., SINGH, K.P.: Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse an agricultural waste. Water Res., 36, 2002, 2304-2318.

MOUTSATSOU, A., PROTONOTARIOS, V.: Production of synthetic zeolites from lignite-calcareous Greek fly ashes and their potential for metals and metalloids retention. In: Waste Management and the Environment III, 49-56. 3rd International Conference on Waste Management and the Environment, Malta, June, 2006.

MURAYAMA, N., YAMAMOTO, H., SHIBATA, J.: Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. Int. J. Miner. Process, 64, 2002, 1-17.

MUSYOKA, N.M., PETRIK, L.F., FATOBA, O.O., HUMS, E.: Synthesis of zeolites from coal fly ash using mine waters. Miner. Eng., 53, 2013, 9-15.

OREN, A.H., KAYA, A.: Factors affecting adsorption characteristics of $Zn^{2+}$ on tow natural zeolites. J. Hazard. Mater., 131, 2006, 59-65.

QIU, W., ZHENG, Y.: Removal of lead, copper, nickel, cobalt, and zinc from water by a cancrinite-type zeolite synthetized from fly ash. Chem. Eng. J., 145, 2009, 483-488.

QUEROL, X., UMAÑA, J.C., PLANA, F., ALASTUEY, A., LÓPEZ-SOLER, A., MEDINACELI, A., VALERO, A., DOMINGO, M.J., GARCIA-ROJO, E.: Synthesis of zeolites from fly ash at pilot plant scale. Examples of potential applications. Fuel, 80, 2001, 857-865.

QUEROL, X.: Synthesis of zeolites from coal fly ash: an overview. Int. J. Coal Geol., 50, 2002, 413–423.

RAJEC, P., MÁTEL, Ľ., ORECHOVSKÁ, J., ŠÚCHA, J., NOVÁK, I.: Sorption of radionuclides on inorganic sorbents. J. Radioanal. Nucl. Chem., 208, 1996, 477-486.

RAO, G.P.C., SATYAVENI, S., RAMESH, A., SESHAIAH, K., MURTHY, K.S.N., CHOUDARY, N.V.: Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite. J. Environ. Manag., 81, 2006, 265-272.

REMENÁROVÁ, L., PIPÍŠKA, M., FLORKOVÁ, E., HORNÍK, M., ROZLOŽNÍK, M., AUGUSTÍN, J.: Zeolites from coal fly ash as efficient sorbents for cadmium ions. Clean Technol. Environ. Policy, 2014, DOI 10.1007/s10098-014-0728-5.

RÍOS, C.A.R., WILLIAMS, C.D., ROBERTS, C.L.: A comparative study of two methods for the synthesis of fly ash-based sodium and potassium type zeolites. Fuel, 88, 2009,1403-1416.

SHIGEMOTO, N., HAYASHI, H., MIYAURA, K.: Selective formation of Na–X zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction. J. Mater. Sci., 28, 1993, 4781–4786.

SPRYNSKYY, M., BUSZEWSKI, B., TERZYK, A.P., NAMIEŚNIK, J.: Study of the selection mechanism of heavy metal ($Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Cd^{2+}$) adsorption on clinoptilolite. J. Colloid Interface Sci., 304, 2006, 21-28.

WANG, C., LI, J., SUN, X., WANG, L.: Evaluation of zeolites synthetized from fly ash as potential adsorbents for wastewater containing heavy metals. J. Environ. Sci., 21, 2009, 127-136.

YILDIZ, B., ERTEN, H.N., KIŞ, M.: The sorption behaviour of $Cs^+$ ion on clay minerals and zeolite in radioactive waste management: sorption kinetics and thermodynamics. J. Radioanal. Nucl. Chem., 288, 2011, 475-483.

ZIYATH, A.M., MAHBUB, P., GOONETILLEKE, A., ADEBAJO, M.O., KOKOT, S., OLOYEDE, A.: Influence of physical and chemical parameters on the treatment of heavy metals in polluted stormwater using zeolite – a review. J. Water Resour. Protect., 3, 2011, 758-767.