



FLY ASH-DERIVED ZEOLITES AS ADSORBENTS FOR Ni REMOVAL FROM WASTE WATER

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The fly ash originating from power plants is fifth ranked, as importance, among the mineral sources, fact that justifies the increased number of the researches performed in order to find the most suitable techniques for its valorization as adsorbent.

Although the fly ash could be used without any modification, a higher efficiency results when it is transformed in zeolite, by acid or alkaline attack. The possibility of using the synthesized zeolites for heavy metals adsorption, particularly nickel ions from wastewater, was investigated in this work. The composition of fly ash and the reaction conditions, (such as alkali concentration, treatment temperature, curing time, liquid/solid ratio and pH) significantly influence the formation process and the properties of the new synthesized material.

The synthesized materials were characterized using techniques such as scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDAX), X-ray diffraction (XRD) and infrared spectroscopy (IR). The obtained results showed that the alkaline attack procedure can convert fly ash into a beneficial product, which can efficiently remove heavy metals such as nickel from contaminated effluent streams.

INTRODUCTION

The fly ash produced in thermal power plants is a siliceous material that is carried off in the flue gas from which it is usually collected by means of electrostatic precipitators or mechanical collection devices such as cyclones.^{1,2}

Considering the fact that nowadays around 70–75% of the generated fly ash is disposed in landfills various attempts were done in order to reduce the amount of this waste by superior capitalization.^{1,3}

Hence, the fly ash was utilized for the synthesis of the new materials with adsorptive properties⁴ that may be used for different purposes. Among its

different applications we can cite: industrial and wastewater treatment,^{2,4} flue gas desulphurization, extraction of valuable metals, land stabilization from mining areas. It can be also used as fireproof material, as filler material for concrete production.^{5,6} By alkaline attack of fly ash could be obtained geopolymer materials.^{7,8}

The most important property of the fly ash is its increased sorption capacity as a result of the porous structure and high surface area, fact that recommends its usage as sorbent for removal of different pollutants from wastewater.⁹

Thus, the fly ash has been used as a low-cost adsorbent for the removal of lead, zinc, chromium and nickel from aqueous solution.¹⁰⁻¹³ A study

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concerning the removal of heavy metals within a system containing 100 mg/L pollutant and fly ash with particle size equal to 75 μm , as sorbent, in dose of 3.5 g/L led to a process efficiency of 91% for Cr(VI) reached at pH = 6 and 85.6%, respectively, for Ni(II) attained at pH = 8 after a 90 minutes contact period.¹⁰

The conversion of this waste into a new product improved is very attractive. Therefore various researchers^{3,9,14,15} converted fly ash into zeolites that can be used as low-cost adsorbents for heavy metals removal from different matrices.¹⁶

Zeolites are important crystalline aluminosilicates which can occur naturally or may be obtained by chemical synthesis. Earlier zeolites were formed by fusing weighed amounts of feldspar, clay, and soda ash.¹⁰ Capable of undergoing reversible base-exchange reactions¹⁷ the zeolites are used as microporous adsorbents. Natural zeolites generally present a low surface area; however for some of the synthetic ones the apparent surface area¹⁸ can be as high as 700 m^2g^{-1} .

Fly ash composed primarily of aluminosilicate glass, mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and quartz (SiO_2) provide a ready source of Al and Si, which is necessary for the synthesis of zeolites. The zeolites with a low Si/Al ratio have been proved to be excellent adsorbents of heavy metals because of their high cation exchange capacities (CEC) and large pore volumes.^{19,20} The conversion of fly ash into zeolites proves to be effective for removing such metals from wastewater. Several authors have reported the conversion of fly ash into zeolites by the treatment of ash with concentrated NaOH solutions at elevated temperatures.^{16,19,20} Recently, more sophisticated treatments including the use of microwave radiation and fusion with NaOH followed by hydrothermal treatment have been reported.²¹⁻²³ Some works exhibit data regarding the uptake of heavy metals on the fly ash and on zeolites compared to those achieved by using other

commercially available adsorbents.^{10,21-23} The efficiency of fly ash was suggested to be comparable to that of the conventional powdered activated carbon.¹⁰

The textural characterization¹⁸ of zeolites consist in measuring surface area, pore volume, and pore size distribution and it is carried out by using gas (usually nitrogen) adsorption technique.

One of the objectives of this study was to investigate the fly ash conversion into zeolites and to characterize the obtained zeolites by methods such as SEM, IR, EDAX, XRD. Another objective was to investigate the efficiency of nickel removal using the synthesized zeolites. This heavy metal exhibits an increased toxicity. Its uptake on a low cost material may be an attractive possibility for the environment decontamination. Therefore many attempts in this direction were done.

In previous papers,^{11,13,24} good results were observed through a similar investigation performed for the removal of pollutants like lead and Astrazone Blue by adsorption on such kind of materials. The efficiency of nickel removal from aqueous solution when using the zeolites obtained from fly ash will be monitorized and compared to that of other adsorbents such as unmodified fly ash.

RESULTS AND DISCUSSION

Adsorbents characterization

1. Characterization of fly ash

The possibilities to capitalize the fly ash in order to obtain new materials with adsorptive capacities result from its properties that are influenced to a great extent by those of the coal burned and by the techniques used for handling and storage.

Table 1

Composition of coal ash, EDX

Element	Wt, %	At,%
C	14.87	25.41
N	5.26	7.71
O	20.58	26.41
Mg	0.78	0.66
Al	8.31	6.32
Si	37.41	27.35
P	0.46	0.31
K	0.72	0.38
Ca	7.69	3.94
Ti	1.40	0.60
Fe	2.52	0.93

The elemental analysis demonstrated that this fly ash contains important quantities of Si, O, Al, Ca, Fe, K, Mg, N as principal elements and small quantities of Ti and P (Table 1). This results are consistent with literature reported data with the exception of C for which the losses to calcinations indicated a higher content^{2,20,21,24} Based on the chemical composition obtained from EDX analysis, this fly ash are classified in Class F.^{1,2,4,24}

From the SEM analysis one may observe that the ash particles exhibit irregular shapes due to the presence of a relative high amount of unburned

carbon (Fig. 1). At the same time, the results of the granulometric distribution revealed a quite small fraction of ash with less than 40 μm particles.

The chemical analysis allows the determination of elementary or oxide compounds in the material, but it does not give any information about “mineralogical” composition of the fly ash. To get some further information about the way the oxide compounds bond, we have performed the XRD analysis (Fig. 2).

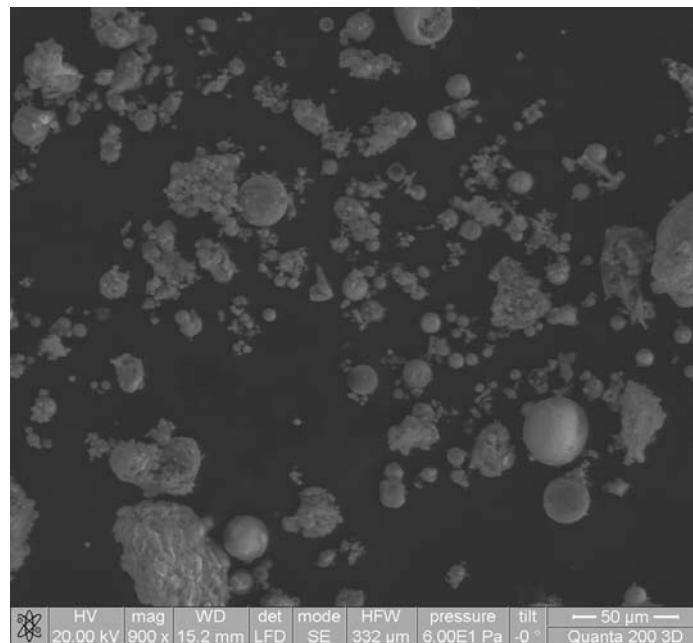


Fig. 1 – Scanning electronic microscopy image for fly ash.

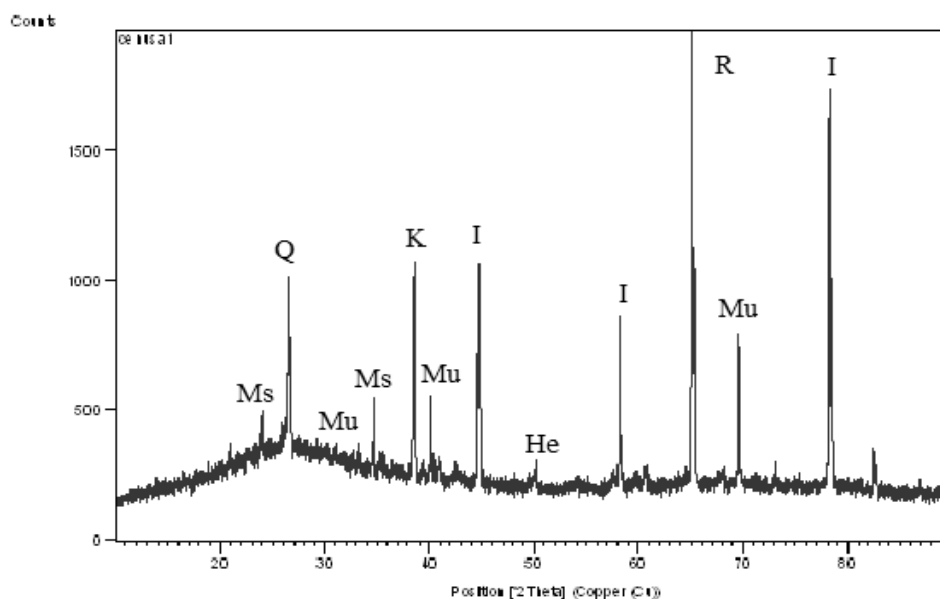


Fig. 2 – X-ray diffractogram of the fly ash used as absorbent for Ni^{2+} .

Table 2
Composition of zeolite, EDX, Wt %

Element	Z1	Z2	Z3
C	13.28	13.25	14.69
N	6.98	6.63	6.92
O	24.05	24.55	24.24
Na	4.12	5.94	4.75
Mg	0.69	0.84	0.76
Al	9.56	9.12	8.66
Si	33.16	32.18	32.58
K	1.28	1.56	1.40
Ca	2.23	2.08	2.13
Ti	0.75	0.82	0.74
Fe	4.04	3.04	3.14

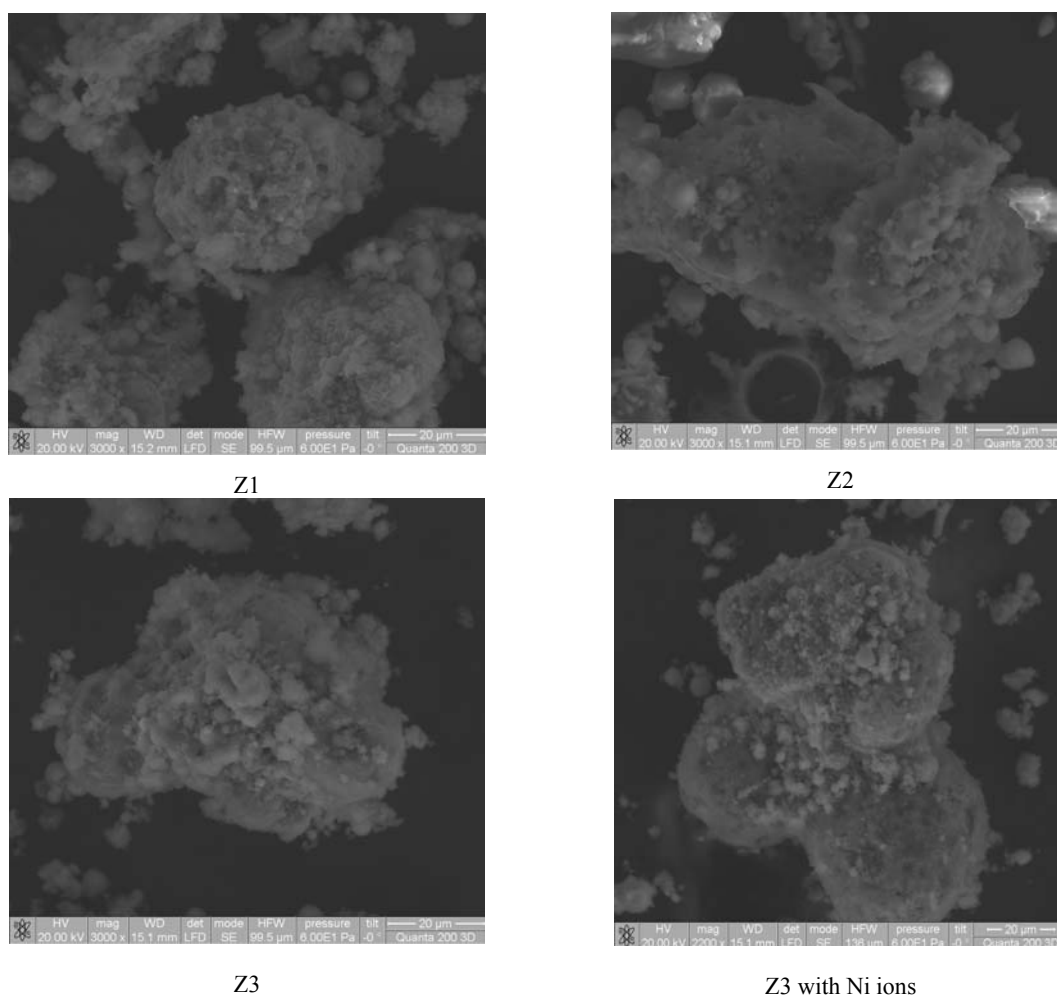


Fig. 3 – Scanning electronic microscopy image for synthesized zeolite.

The XRD analyses show that the ash contains crystalline phases such as: illite (I), kaolinite (K), mullite (Mu), hematite (He), muscovite (Ms), rutile (R) and glassy phase.

2. Characterization of zeolites

The synthesized zeolites were chemically analyzed and their composition is presented in Table 2. The analysis shows that the main

constitutive elements of the zeolites are: C, Si, O, Al, Ca, Fe, Na, K, N, Ti and Mg with the mention that the last two elements were presented only in small quantities. Taking into account that the synthesis has been performed with sodium hydroxide, the calcium content decreases since this element was replaced by sodium within the zeolite structure.

From SEM images it can be observed that zeolite presents modified particles (Fig. 3) compared to the fly ash (Fig. 1). The unmodified ash consists of spherical and irregular shaped particles while the zeolite has marked changes in the surface morphology due to the alkali activation.

The presence of large amount of regular crystal particles on the surface of product particles indicates high conversion of the raw ash into crystalline zeolites. Transformation degrees depend on zeolitisation conditions, this fact being illustrated in Fig. 3.

IR spectra (Fig. 4) performed for the synthesized zeolites indicate that the most relevant band is observed in the 950-1100 cm^{-1} range, corresponding to an intense Si (Al)-O band. The characteristic IR vibration bands of the zeolite materials are as follows: 3700-3600 cm^{-1} – stretching vibration –OH; 3600-2200 cm^{-1} –

stretching vibration –OH, HOH; 1200-950 (s) cm^{-1} – asymmetric stretching Si-O-Si and Al-O-Si, 850 cm^{-1} - Si-O stretching, OH bending (Si-OH); 795 cm^{-1} – symmetric stretching (Si-O-Si); 688 cm^{-1} – symmetric stretching (Si-O-Si and Al-O-Si) and 424 cm^{-1} – bending (Si-O-Si and O-Si-O).

Fig. 5 shows the XRD patterns of the zeolites obtained by fly ash alkaline conversion at 80°C for different periods. The intense diffraction peak at 26.65° can be attributed to Faujasite-Na. The results revealed that a single zeolite phase can be obtained through hydrothermal zeolite synthesis. The peak intensity of α -quartz and mullite is almost unchanged, confirming that the crystalline phases in zeolite materials are not dissolved during the aging.

IR (Fig. 4) and XRD (Fig. 5) analyses confirmed the formation of the Na-zeolite.

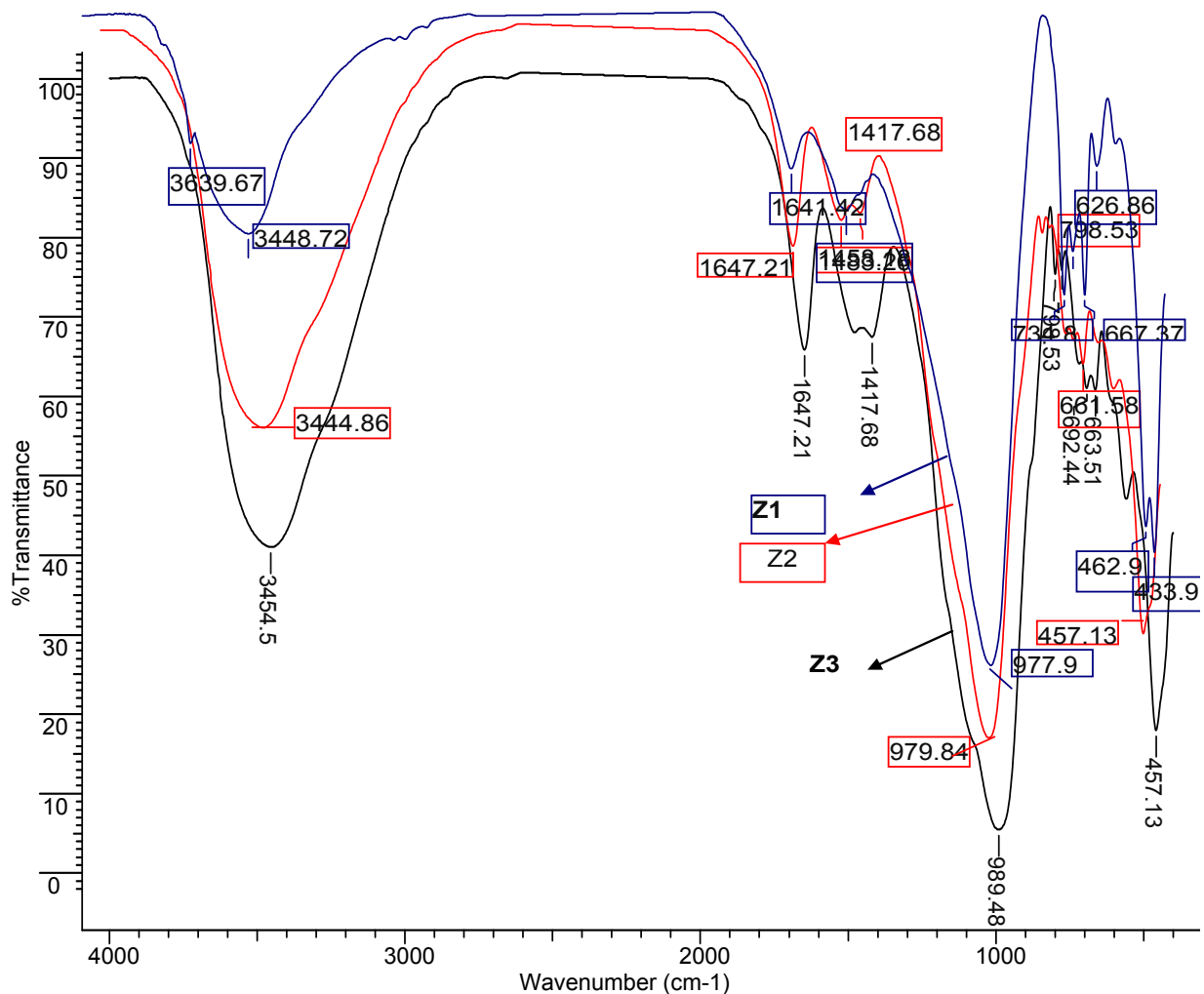


Fig. 4 – Zeolites IR spectra.

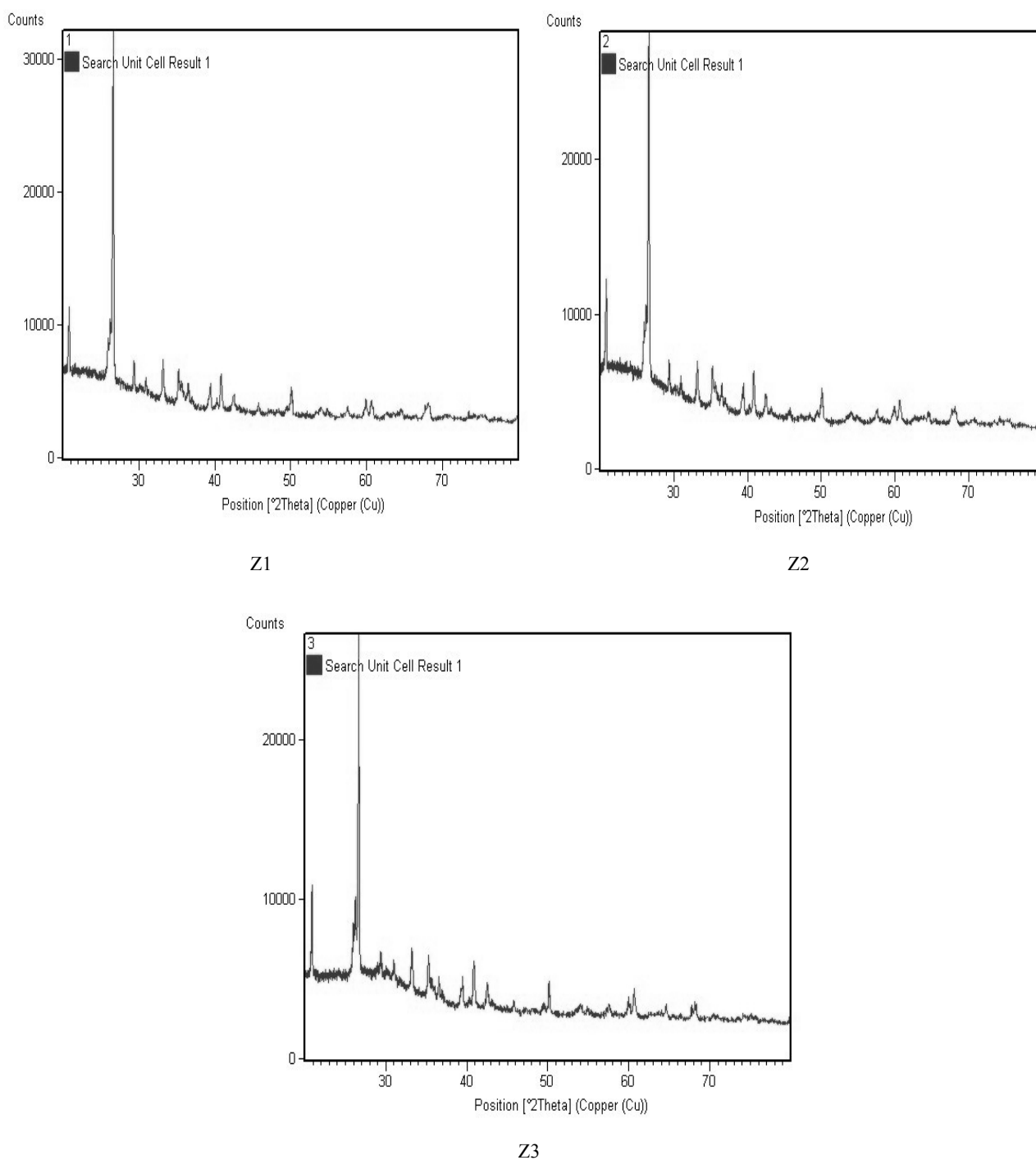


Fig. 5 – Zeolites X-ray diffractogram.

Researches on the removal of Ni²⁺ ions from solutions

The experimental researches were aimed to establish the percent of Ni²⁺ removal from solutions by adsorption.

pH of solution is an important factor that influences the removal of Ni(II) from aqueous

solution by the use of a zeolite. The removal of Ni(II) increases slowly at pH ranging from 2.0 to 4.0, then increases sharply at pH 4.0 – 6.0, being maintained at high level at pH > 6.0 when about 85% of Ni(II) is adsorbed on the zeolite. It is well-known that the species of Ni(II) in aqueous solution are important for its sorption due to the fact that these species are strongly dependent on

pH values.²⁵ Ni(II) can be present as Ni^{2+} , $\text{Ni}(\text{OH})^+$, $\text{Ni}(\text{OH})_2$, $\text{Ni}(\text{OH})_3^-$ and $\text{Ni}(\text{OH})_4^{2-}$ species at different pH values. At low pH values, Ni^{2+} and $\text{Ni}(\text{OH})^+$ are the main species of Ni(II) in aqueous solution.²⁵ The removal of Ni^{2+} and $\text{Ni}(\text{OH})^+$ is difficult as a result of the electrostatic repulsion at pH range 2.0 – 4.0. At high pH values, the concentration of active sites increases. This behavior is expected for many metal ions including nickel.^{11,13,25,26} The influence of pH can be related with the fact that in an acid environment competition between metals and H^+ ions occurs and the metal retention in such condition is not significant. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites, fact that results in an enhancement of metal adsorption.^{27,28}

The results of this study confirmed that pH is one of the most important factors which control the nickel adsorption. The smallest value of removal efficiency (20%) on zeolite Z3 was registered at pH = 2, while the maximum percentage of Ni removal (98%) resulted at pH 6. An increased removal efficiency is attained also at pH = 4, but the maximum value was reached after 180 minutes compared to the case of pH = 6 when the maximum value was obtained after only 90 minutes of adsorption. However, the process appears to be very fast at the beginning since a big amount of nickel has been retained in the first 30 minutes. The removal efficiency decreased at 80% at pH = 8 (Fig. 6).

A comparison between the adsorption on Z3 and on unmodified ash was performed for different pH values. The result of the adsorption process conducted at pH = 8 evidenced the fact that the Ni ions were hardly removed, whereas at pH = 4, a removal efficiency of 40% on Z2 and of 10% on unmodified fly ash were reached after 90 minutes (Fig. 7).

For the same zeolite Z3 and at the same duration of the process, at pH 6, the removal efficiency increased at 93%, while on the unmodified fly ash Ni removal increased at only 30%, Fig. 8.

On the other hand one may observe a removal efficiency of 70% within the first 10 minutes of contact between the Ni ions and the zeolite.

The relatively high value of the removal efficiency suggests the coexistence of several removal processes such as ion exchange, electrostatic attraction, Van der Waals interactions and precipitation.

Data concerning the influence of pH on the removal of Ni^{2+} were reported in previous paper.¹³⁻¹⁵

For analyzing the adsorption capacity (removal efficiency) of other types of zeolites, we performed experiments using Z1 and Z2, at the pH values of 2, 4 and 6, the results being presented in Figs. 9 and 10.

Both zeolites presented high adsorption capacity for nickel ions, but zeolite Z2 exhibited the maximum value (98%) after 60 min.

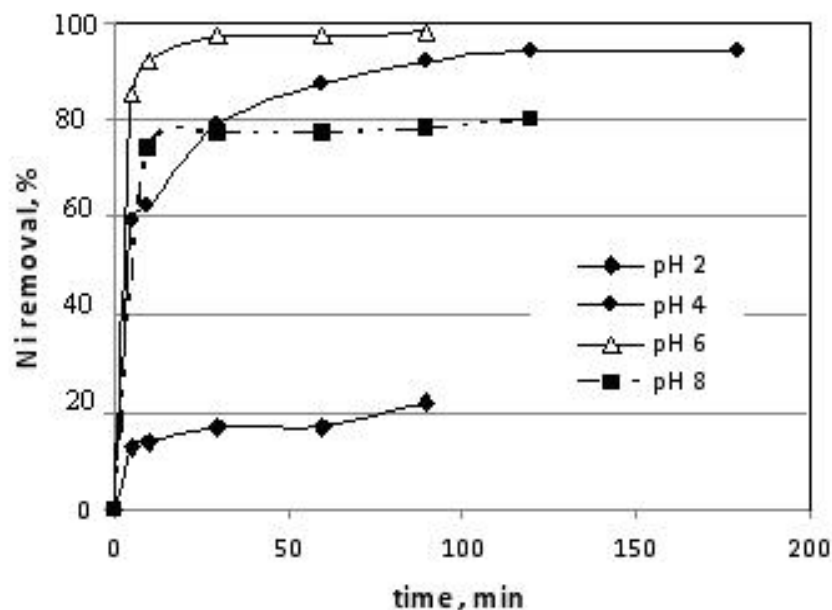


Fig. 6 – Influence of pH on the Ni^{2+} removal efficiency onto Z3.

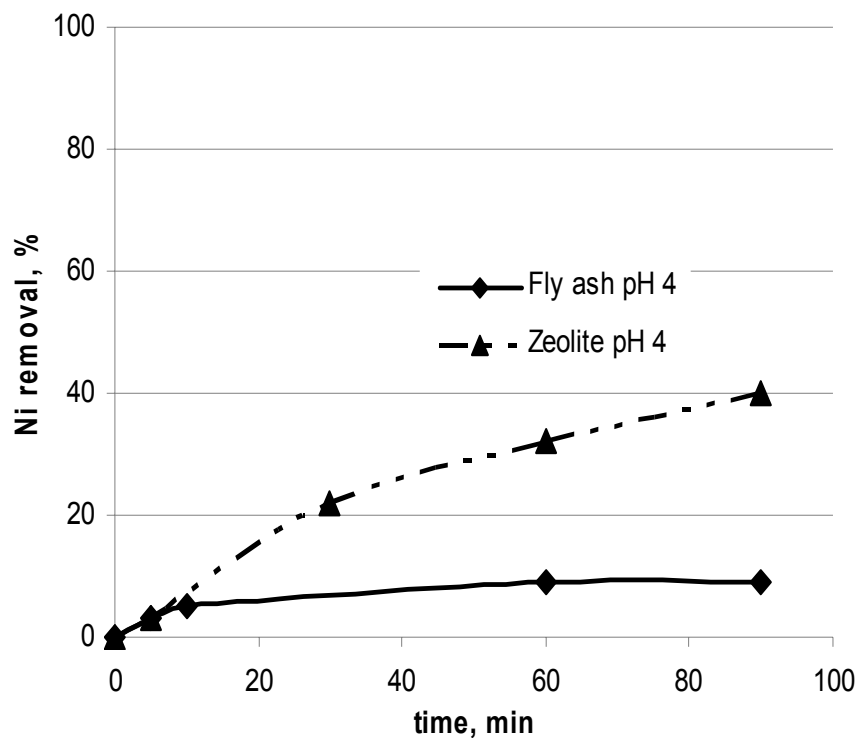


Fig. 7 – Removal efficiency of Ni^{2+} ions on the unmodified ash and on Z2, respectively, at pH 4.

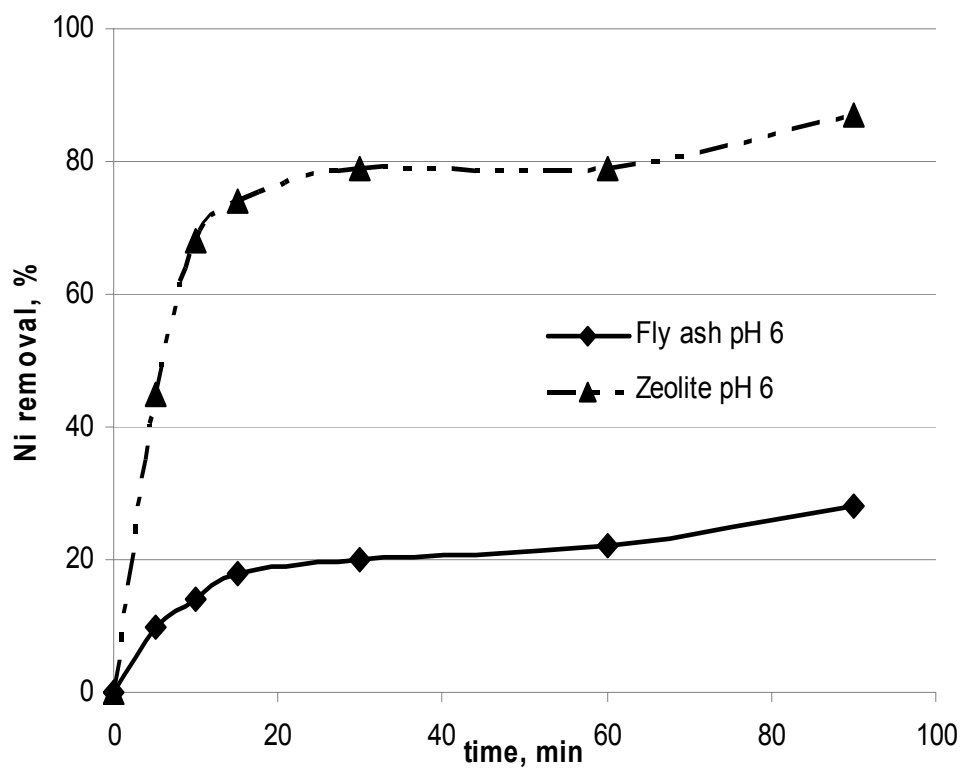


Fig. 8 – Removal efficiency of Ni^{2+} ions on the unmodified ash and Z3, respectively, at pH 6.

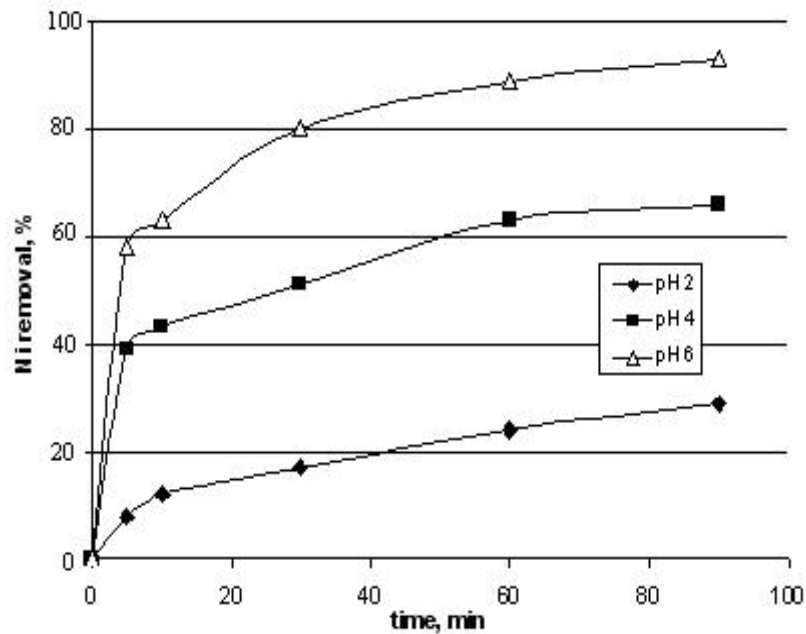


Fig. 9 – Removal efficiency of Ni²⁺ ions onto Z1.

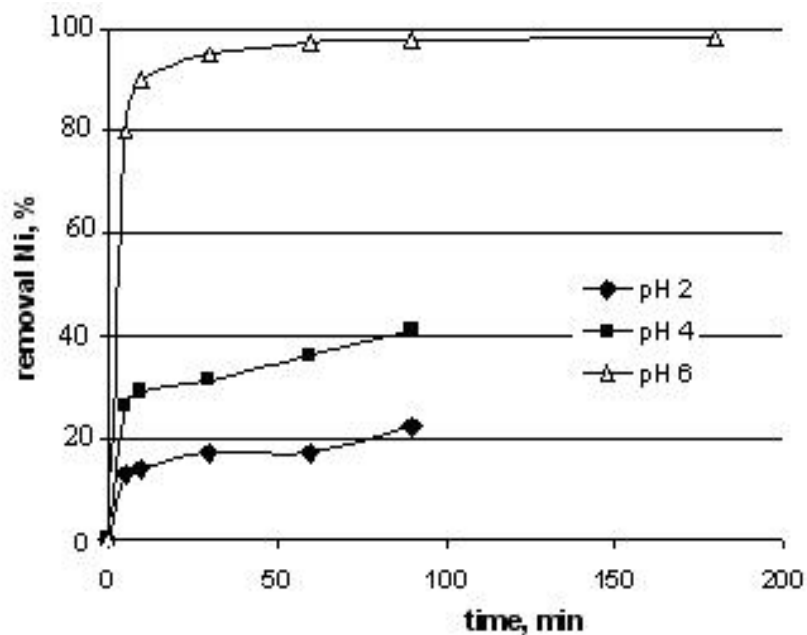


Fig. 10 – Removal efficiency of Ni²⁺ ions onto Z2.

In order to establish the influence of zeolitization conditions over the adsorption capacity, the process was conducted on unmodified fly ash as well as on the synthesized materials at pH = 6 (when the removal efficiency appeared to be the highest), Fig. 11.

The results show that the removal of nickel is influenced by the type of materials, respectively of the zeolitization conditions. Maximum value of removal efficiency is presented by Z2, obtained in system subjected to stirring for 8 hours. Decrease

of zeolitization time, or absence of stirring determines the decrease of removal efficiency.

The three types of zeolites have different adsorption capacities due to the ion exchange capacity, which depends on the Sodium content. Zeolite Z2 has the highest adsorption capacity fact that can be explained by the greater sodium content compared to that of zeolites Z1 and Z3 (Table 2).

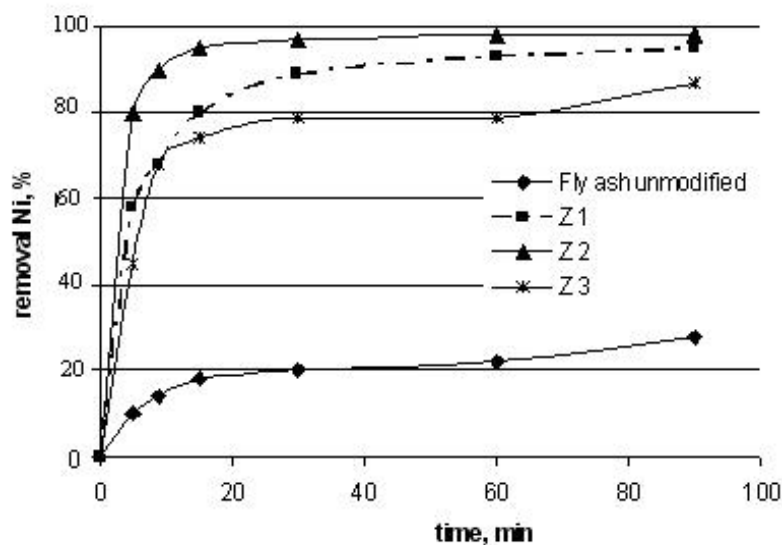


Fig. 11 – Ni²⁺ removal efficiencies on different materials, at pH 6.

EXPERIMENTAL

The material used in this study is the ash, a waste product resulted in thermal power plant from burning of pit coal. About 5 kg of ash samples (fly ash and bottom ash) have been manually collected for seven consecutive days at different sites from the warehouse of a power plant located in Iași, Roumania.

Z 1	10g fly ash + 30 mL NaOH	1/3	80 °C (without stirring)	8 hours
Z 2	10g fly ash + 30 mL NaOH	1/3	80 °C (with stirring)	8 hours
Z 3	10g fly ash + 30 mL NaOH	1/3	80 °C (with stirring)	4 hours

The fly ash and the zeolite were characterized using the following equipments: SEM/EDX for morphological and elemental analysis of the samples, QUANTA 3D - AL99/D8229; Diffractometer X'PERT PRO MRD, with Cu K α radiation source and operated at 45 kV/40 mA, XRD data were collected under the same experimental conditions; in the angular range $3^\circ \leq 2\theta \leq 80^\circ$ with counting time 47 m 37 s; for FT-IR analysis - DIGILAB FTS 2000; Multi-Parameter Consort C831 (pH, mV, C, Conductivity), pH 0-14, conductivity 0 - 200 mS, temperature 0 - 100°C.

For nickel analysis it was used the atomic absorption spectroscopy with Buck Scientific AAS equipment.

The equipment used for studying the removal efficiency consisted in a vessel where the liquid was subjected to magnetic stirring; a pH-meter that contained also the referring electrode and a conductometer with sounder. A conductometer cell made of glass and exhibiting a bell shape, as well as a potentiometric cell, containing an H-selective electrode manufactured by glass and a calomel electrode were used for this study. The heavy metal ion used within this investigation was the Ni²⁺ ion from a nickel nitrate solution of 0.1 mol/L. The ash/solution ratio was equal to 1/50 for the considered pH values. At certain time intervals, samples were collected, filtered and analyzed by atomic absorption in order to establish the content of nickel ions.

The removal efficiency was calculated with the (Eq. 1):

$$R\% = \frac{m_0 - m}{m_0} \cdot 100 \quad (1)$$

Zeolite materials were obtained by direct alkaline conversion processes in autoclaves at 353 K and different treatment intervals: 4h and 8h. The fly ash was added to a NaOH solution 2M. The zeolites obtained were filtered, washed and dried for 4 hours at 373 K. The experimental conditions were the following:

where m_0 – pollutant mass, in solution, at the initial moment (mg) and m – pollutant mass, in solution, at the sampling time (mg).

CONCLUSIONS

The possibility of using the synthesized zeolites for heavy metals adsorption, particularly nickel ions from wastewater, was investigated in this work.

Based on the experimental results, we concluded that the ash used for this purpose, which resulted from combustion of pit coal, belongs to the F class.

Faujasite-Na zeolites have been prepared by a hydrothermal treatment of the fly ash with NaOH. Hence, zeolite or geopolymer results from alkaline attack depending on synthesis conditions.

The nickel adsorption from aqueous solution by these modified ashes was found to occur readily. Faujasite-Na zeolite (Z2) was more efficient in removing Ni than Faujasite-Na zeolites (Z1 and Z3), at pH = 6, but all types of zeolites were more efficient compared to the original ash. The synthesized products show a greater adsorption

capacity than similar materials reported in other studies.

The pH is one of the most important factors which control the nickel adsorption. The smallest value of the removal efficiency (20 %) was registered at pH= 2 while the maximum removal percent resulted for values of pH 6, for Z3. Although high process efficiency results also at pH = 4, this is obtained after a twofold duration of time. The process appears as being very fast at the beginning since a big amount of nickel is retained in the first 30 minutes.

It is evident that this alkaline attack procedure can convert fly ash into a beneficial product, which can efficiently remove heavy metals such as nickel from contaminated effluent streams.

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