Research article

Removal of heavy metals from wastewater using CFB-coal fly ash zeolitic materials

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ABSTRACT

Polish bituminous (PB) and South African (SA) coal fly ash (FA) samples, derived from pilot-scale circulated fluidized bed (CFB) combustion facilities, were utilized as raw materials for the synthesis of zeolitic products. The two FAs underwent a hydrothermal activation with 1 M NaOH solution. Two different FA/NaOH solution/ratios (50, 100 g/L) were applied for each sample and several zeolitic materials were formed. The experimental products were characterized by means of X-ray diffraction (XRD) and energy dispersive X-ray coupled–scanning electron microscope (EDX/SEM), while X-ray fluorescence (XRF) was applied for the determination of their chemical composition. The zeolitic products were also evaluated in terms of their cation exchange capacity (CEC), specific surface area (SSA), specific gravity (SG), particle size distribution (PSD), pH and the range of their micro- and macroporosity. Afterwards the hybrid materials were tested for their ability of adsorbing Cr, Pb, Ni, Cu, Cd and Zn from contaminated liquids. Main parameters for the precipitation of the heavy metals, as it was concluded from the experimental results, are the mineralogical composition of the initial fly ashes, as well as the type and the amount of the produced zeolite and specifically the mechanism by which the metals ions are hold on the substrate.

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1. Introduction

The combustion of solid fuels using conventional technologies dominates the coal-burning power production. However, more environmental-friendly technologies, such as the CFB combustion technology, continuously gain ground. Therefore, the amounts of CFB-derived coal fly ash, are steadily increasing, as a result of the continuous development of the CFB technologies [1]. It is obvious that alternative applications should be developed in order to recycle the high FA output [2]. The production of zeolites is one of the potential applications of fly ash in order to obtain high value industrial products with environmental technology utilization. The synthesis of zeolite products from fly ash is analogous to the formation of natural zeolites from volcanic deposits or other high-Si–Al materials [3,4]. Both volcanic ash and FA are fine-grained and contain a large amount of active aluminosilicate glass. One of the processes from which zeolites can be naturally formed is through the influence of hot groundwater on the glass fraction of volcanic ash. The particular zeolitic development may take thousands of years in order to form natural zeolites. In the laboratory the process can be speeded up (to days or hours) for both volcanic ash and FA. In that case the activation solution is an alkaline one, usually NaOH or KOH. The classical alkaline conversion of fly ash is based on the combination of different activation solution/FA ratios, with temperature, pressure and reaction time to obtain different zeolitic types. 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 [5,6]. NaOH or KOH solutions with different molarities, at atmospheric and water vapor pressure, from 80 to 200 °C and 3 to 96 h have been combined to synthesize many different types of zeolites. The zeolitic content of the resulting products varies depending on the solution/fly ash ratio applied and on their reaction time [7]. All the aforementioned procedures utilize coal fly ash from conventional combustion and very little research has been conducted on the field of CFB-derived coal FA utilization. The present study deals with the hydrothermal activation of two coal FAs produced in pilot-scale CFB combustion facilities and aims at testing the synthetic products for their potential to be used as low-cost adsorbents for the removal of heavy metals from industrial wastewater. The traditional treatment methods of the heavy-metal contaminated aquatic environments, such as the reduction precipitation, the ion exchange, the electrochemical reduction, the reverse osmosis, etc., are methods that involve large exposed liquid sur-

Table 1
The effect of alkaline hydrothermal activation on the composition of the major chemical compounds of CFB-fly ashes.

Compound	Before hydrothermal activation		After hydrothermal activation			
	PB-FA	SA-FA	PB-FA (50 g/L)	PB-FA (100 g/L)	SA-FA (50 g/L)	SA-FA (100 g/L)
SiO_2	38.99	48.94	29.43	30.35	37.03	36.82
Al_2O_3	25.39	34.71	12.59	14.14	20.58	20.87
Na_2O	1.70	0.35	6.43	4.18	9.71	9.52
SO_3	8.82	5.59	0.96	0.80	0.43	0.66
CaO	17.54	10.12	20.61	20.33	11.95	11.75

face area and long detention periods as well as high capital cost, usually not-affordable for small-scale industries. Thus, the cost-effective disposal of heavy metal-containing wastewater remains a challenging task for industrialists and environmentalists [8,9].

2. Materials and methods

PB-FA and SA-FA derived from CFB facilities underwent an alkaline hydrothermal treatment at 90 °C, using NaOH 1 M as an activation solution, in a 1 L stainless steel reactor. The incubation period was set at 24 h and mixing took place at 150 rounds per minute (rpm). After that period, the mixture was filtered and the solid residue was dried at 40 °C for 24 h and leached with water until no NaOH was detected. Chemical analyses of PB- and SA-CFB-FAs as raw material as well as zeolitic products were performed by X-ray fluorescence (XRF). The mineralogical composition of the zeolitic materials was identified by X-ray diffraction (XRD) and scanning electron microscope (SEM). The synthetic zeolitic materials were subjected to N_2 adsorption using BET method in order to determine their specific surface area (SSA), while their cation exchange capacity (CEC) was evaluated following the US EPA 9081 method (sodium acetate). The particle size distribution (PSD) of the initial FAs and the synthesized zeolitic materials was determined by MalVern Mastersizer-S using the wet dispersion method in water. The study of the range of macro- and microporosity in the synthetic zeolitic materials was performed using a porosimeter Autosorb-1 (with crypton analysis, optimum for microporosity) made by Quanta-Chrome. Furthermore, the pH (ISO 6588) and the specific gravity (SG-ASTM C642) of the initial FAs and the synthetic zeolitic materials were also evaluated. In order to test the synthetic zeolitic materials for their capability of removing heavy metals from wastewater, an aqueous solution of 1000 mg/L (each) of Cr, Cu, Ni, Pb, Zn and 100 mg/L Cd was prepared. The procedure involved filling a series of glass tubes with 50 mL of solution, adding 10 g of adsorbent to them and then implementing mechanical stirring at 200 rpm. Although the incubation period was set at 24 h, the preliminary investigations showed that the uptake of all the examined metals, by all the zeolitic materials, was completed within 2 h, since

Table 2
Mineralogical phases identified in the synthetic zeolitic materials (+: presence of mineral phase, −: absence of mineral phase).

Mineral	PB-FA (50 g/L)	PB-FA (100 g/L)	SA-FA (50 g/L)	SA-FA (100 g/L)
Quartz	+	+	+	+
Calcite	+	+	+	+
Magadiite	+	+	−	−
Lime	+	+	−	−
Hematite	+	+	+	+
Portlandite	+	+	+	+
Illite	+	+	−	−
Zeolite A (Na)	−	−	+	+
Zeolite A (K)	−	−	+	+
Unnamed Zeolite	+	+	−	−
ZSM-18	+	+	−	−
Linde (L)	−	+	−	−
Erionite	+	+	+	−

no practical change was detected up to the period of 24 h. Afterwards, the supernatant solution was filtered and subjected to flame atomic adsorption spectroscopy (FAAS). The process was repeated for three times and the average measured values are given as the final results of the (%) heavy-metal uptake by the zeolitic materials. The standard deviation for the uptake of metals lies within a small range: presents a minimum in the case of Ni (0.01%) and reaches a maximum on the occasion of Cr (0.025%)

3. Results and discussion

3.1. Synthetic procedure of zeolitic materials and their characterization

3.1.1. Chemical composition

NaOH (1 M) solution was selected as activation solution, since it presents higher conversion efficiency than KOH, under the same temperature. The experimental conditions (NaOH concentration, temperature) are typical for pure alkaline activation, taking place at low temperatures and intermediate activation periods [10,11,12]. The applied techniques mainly aim at the dissolution of Al–Si bearing phases of FA and the subsequent precipitation of the zeolitic materials. Table 1 illustrates the impact of the alkaline activation on the chemical composition of the raw materials (CFB-fly ashes), which is profound concerning the analogous reduction in the percentages of SiO_2 and Al_2O_3. The effect of NaOH on the alumino-silicate materials is tremendously intense, mainly because of the presence of aluminum. In fact, it causes differentiation in the distribution of the electric charge between the Al–O and Si–O bonds that results in the polarization of the chemical bonds and the enhancement of the chemically active centres (of positive and negative charge) in the lattice. Thus, terminal groups such as ≡Si–OH, ≡Si–ONa, ≡Si–O–, (≡Si–O)3Al–O– are developed and, along with NaOH, lead to the formation of more complex products (i.e. zeolites) [13–16]. Therefore, NaOH solutions present higher conversion efficiency than the respective KOH under the same temperature, as it is also concluded from the vast body [3–8,10–12] of previous research studies.

3.1.2. Mineralogical composition and microstructure

The final solid products were subjected to mineralogical analysis for the identification of known zeolites. The results are presented in Table 2; in this table there can also be found the rest identified phases that are attributed to the initial fly ashes. The formation of the aforementioned zeolitic products was also confirmed by SEM investigation (Figs. 1–6). In Figs. 1 and 2 the zeolitic grains of PB-FA treated samples (included in Table 2) can be clearly observed. Figs. 3–6 include the SEM photos of the alkaline-treated SA-FA (50 and 100 g/L FA/NaOH ratios), where the cubic structures refer to Zeolite-A. That fact was confirmed after examining the chemical composition of the synthetic zeolitic materials in respect with their microstructural formation by means of EDAX-coupled SEM (Figs. 7–10).

Fig. 7 presents a cluster of cubic zeolitic crystals of the hybrid product formed after the treatment of SA-FA. It is clear, from
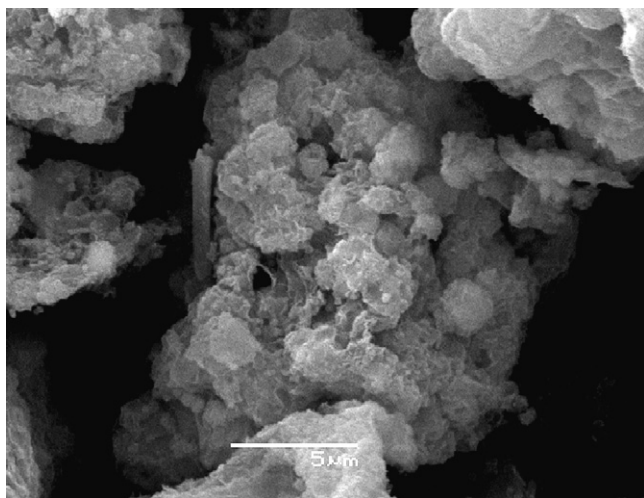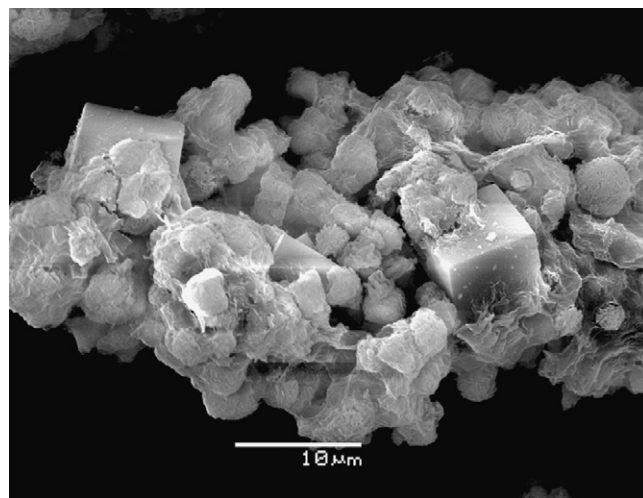
Fig. 1. SEM photo of PB, 50 g FA/1 L NaOH-analysis.

Fig. 4. SEM photo of SA, 100 g FA/1 L NaOH-analysis.
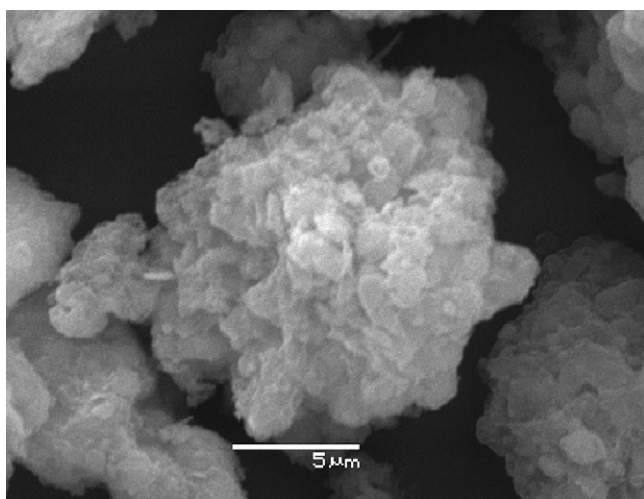

Fig. 2. SEM photo of PB, 100 g FA/1 L NaOH-analysis.
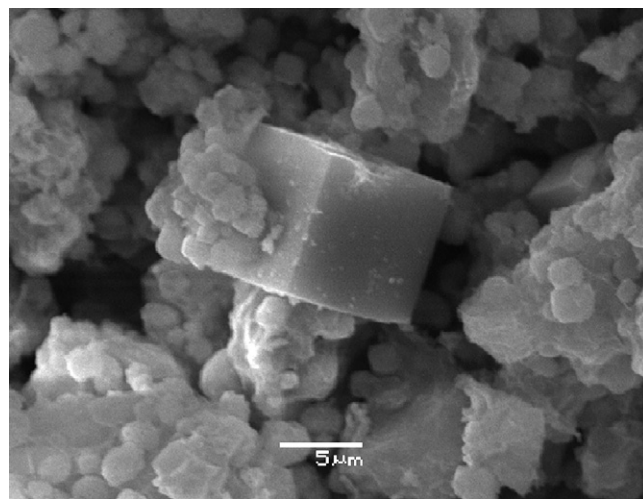

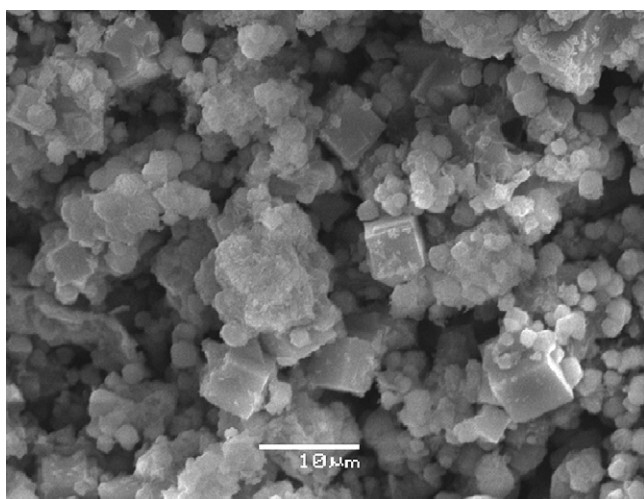**Fig. 5.** SEM photo of SA, 50 g FA/1 L NaOH-analysis.

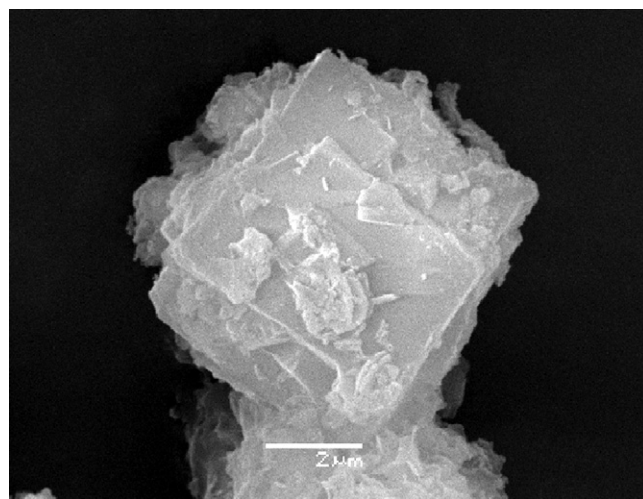**Fig. 3.** SEM photo of SA, 100 g FA/1 L NaOH-analysis.

Fig. 6. SEM photo of SA, 100 g FA/1 L NaOH-analysis.

their chemical composition, that the particular Na- and K-Zeolite-A structures are strongly siliceous. Apart from that, it can be inferred from the low percentage presence of CaO that the alkaline solution consumed a huge amount of cenospheres of fly ash. The cubic crystal included in Fig. 8 was detected in the same zeolitic material. Actually, it seems that either a cluster of cenospheres had been stuck on the one side of the zeolitic crystal or that a group of cenospheres had not had the time available to react with the activation solution. After further EDAX analysis of each single side of this cube, which revealed a substantial difference between their chemical compositions, it was concluded that this variation can be attributed to the escalated presence of apparent remaining parts of the raw material (FA) in the hybrid zeoltic product. Fig. 9 demonstrates a part of the zeolitic material that was developed through the treatment of the same fly ash and, apart from Zeolite A, it also contains Erionite. From the SEM photo of that figure, important conclusions can be drawn, regarding the mechanism of the zeolitic formation. Generally, as the main mass of fly ash is consumed by the alkaline solution, from the internal part of the raw material come out cubic zeolitic structures (circularly marked spot in Fig. 9). Even in this case, the vast body of the zeolitic materials consists of SiO_2 and Al_2O_3. In fact, the percentage presence of the rest major compounds is considerably low (except Na_2O due to the excess of the NaOH activation solution) thus indicating the high level of purity of the synthetic zeolitic materials. The same structure, in further analysis (1 μm) focused on the remaining cenosphere, is demonstrated in Fig. 10. Regarding the chemical composition of the cenosphere, which is also presented in that figure, the relatively high levels of SO_4 and CaO are attributed to the type of the initial FA (CFB-derived FAs usually contain huge percentages of sulphur oxides on account of the fact that the processes of the desulphurization of the flue gases and the combustion of fuel take place simultaneously).

3.1.3. pH values

The pH values of PB-FA and SA-FA along with those of the synthetic zeolitic materials were evaluated and plotted as a function of FA/NaOH ratio (Fig. 11). The pH is an important parameter considering the possible future utilization of the zeolitic materials in the field of wastewater treatment. In both cases of the CFB-coal fly ashes, pH was higher than this of the initial FAs, due to the excess of the alkali concentration, as it is concluded from Table 1. Actually, the higher pH values were measured for the SA-FA zeolitic material activated under the ratio of 50 g FA/1 L NaOH 1 M. The variation of the pH values can be attributed to the chemical processes of the zeolite formation as well as to the regulatory action of the zeolites presented in the final hybrid materials. As it was also experimentally justified, the high pH values of the synthetic materials render them suitable for the uptake of most heavy metals and consequently their utilization for industrial wastewater de-contamination procedures. In fact, the tested metals are immobilized at high pH via the regulation of their solubility. On the other hand, such intensely alkaline materials are usually not appropriate for the precipitation of the – normally mobile at high pH values – Cr(VI). The reduction in the adsorption of Cr(VI) at higher pH is generally attributed to the abundance of OH^- that results in an increased hindrance to the diffusion species and/or to the neutralization of negative surface charge by an excess of hydrogen ions that facilitates the diffusion of dichromate ions and the adsorption on the adsorbent [17–20]. In the current case the hexavalent chromium consists about 0.004 of the total chromium. The rest Cr(III) is very likely to get precipitated by high pH-adsorbents as it was also showed by the current experimental outcomes Section 3.2.

Table 3
CEC values of known zeolites and the synthetic hybrid zeolitic materials.

| Mineral	CEC values (meq/g)
NaP1	1.32
KM	1.72
Analcime	0.61
Kalsilite	0.14
Sodalite	0.50
LindeF	1.74
Cancrinite	0.39
Tobermorite	0.55
K-Chabazite	1.08
Nepheline	0.30
PB-FA (50 g/L)	0.93
PB-FA (100 g/L)	1.20
SA-FA(50 g/L)	0.87
SA-FA (100 g/L)	1.05

3.1.4. Specific gravity, specific surface area and cation exchange capacity

It seems that the hydrothermal treatment of FA had opposing impacts on the specific gravity of the final products. As long as the NaOH solution penetrated the cenospheres of the initial fly ashes, it allowed the trapped air to escape, thus increasing the SG. On the other hand, as the zeolitization process was progressing, the subsequent crystallization of the experimental products yielded to a larger pore volume, thus decreasing the SG. As a result, for PB-FA sample, SG values constantly decreased as FA/NaOH ratio was increasing. On the other hand, regarding SA-FA sample, the lowest SG was for 50 g/L FA/NaOH ratio when it was importantly enhanced for 100 g/L FA/NaOH ratio. Indeed, it almost reached the respective value of the initial FA. Fig. 12 illustrates the evolution of SG as a function of FA/NaOH ratio. Regarding the SSA of the products, it was significantly increased after the alkaline activation, thus enhancing the efficiency of the material, mainly concerning the soil/liquid remediation procedures. In Fig. 13, the comparison of the SSA obtained by the synthetic zeolitic materials is presented. Generally, the results for the treated CFB-fly ashes indicate their upgraded potential of retaining contaminants from polluted soils and liquids. PB-FA activated under the FA/NaOH ratio of 100 g/L shows the highest value of SSA as it was increased to the extent of 220% in respect with the same sample under 50 g FA/L NaOH and to the point of 190% for treated SA-FAs (Fig. 13). The SSA and SG values do not substantially differentiate with those of synthetic zeolitic materials produced by the treatment of calcareous lignite fly ashes [3]. As far as the CEC values of the synthetic zeolitic materials are concerned, the higher (1.2 meq/g) was detected for the case of PB-FA activated under the ratio of 100 g FA/1 L NaOH 1 M. As a matter of fact, although this sample did not present a significant crystallization, it had obtained the better overall properties, among all the other synthetic zeolitic materials, for the procedures of soil/liquid remediation. Fig. 14 describes the comparison of the samples in terms of their cation exchange capacity.

Table 3 includes the CEC values of pure synthetic zeolites [10] as well as those of the hybrid materials produced at the current study. As it can be seen, just four synthetic pure zeolites demonstrate higher CEC values than the highest of the CFB-coal fly ash/zeolitic materials (NaP1, KM, LindeF and Hershellite). Two of them (NaP1 and Linde) identified as part of the hybrid materials of the current study.

3.1.5. Range of porosity and microporosity

The results of the pore characterization of the synthetic zeolitic materials are very encouraging concerning their potential industrial applications. The total pore volume of the material before treatment (normally about 0.01 mL/g) increases significantly after the conversion (up to 0.26 mL/g). Additionally, the synthesized
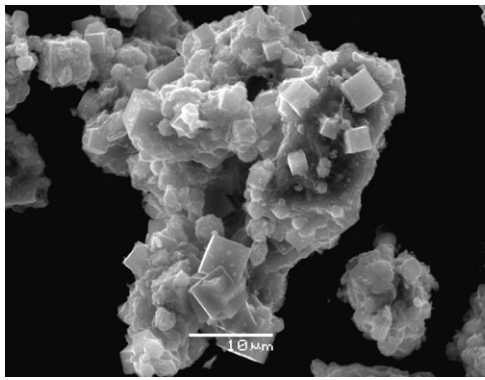
SiO$_2$	56.60
Al$_2$O$_3$	23.27
FeO	0.08
CaO	2.51
Na$_2$O	16.59
K$_2$O	0.07
ZnO	0.36
TiO$_2$	0.20
SO$_4$	0.32

Fig. 7. Cluster of cubic zeolitic crystals raised after the treatment of SA, 100 g FA/1 L NaOH (at left: SEM photo-analysis 10 μm, at right: chemical composition of the cluster).
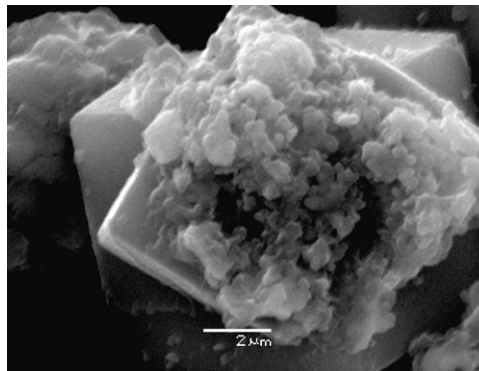

SiO$_2$	42.04
Al$_2$O$_3$	37.21
FeO	0.41
CaO	3.53
Na$_2$O	15.41
K$_2$O	0.41
ZnO	0.31
TiO$_2$	0.14
SO$_4$	0.54

Fig. 8. Cubic zeolitic crystal formed after the treatment of SA, 100 g FA/1 L NaOH (at left: SEM photo-analysis 2 μm, at right: its chemical composition).
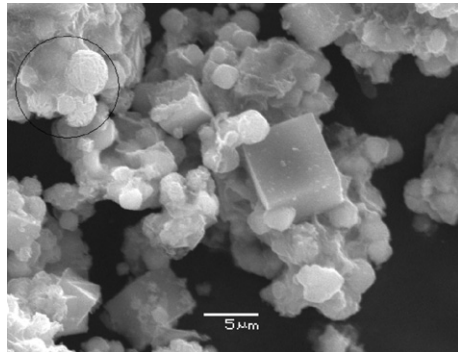
SiO$_2$	42.84
Al$_2$O$_3$	35.6
FeO	0.1
CaO	0.91
Na$_2$O	20.17
K$_2$O	0.14
ZnO	0.12
TiO$_2$	0.05
SO$_4$	0.07

Fig. 9. Cubic zeolitic crystals surrounded by the remaining cenospheres of fly ash. They were formed after the treatment of SA-FA, 50 g FA/1 L NaOH (at left: SEM photo-analysis 5 μm, at right: their chemical composition).
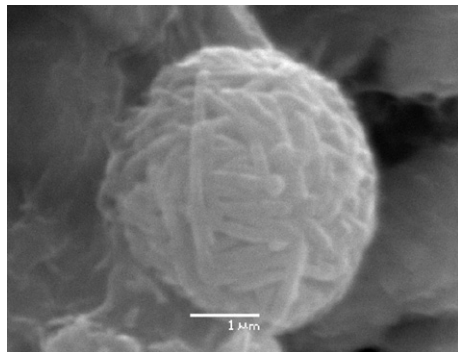
SiO$_2$	41.7
Al$_2$O$_3$	32.4
FeO	0.21
CaO	2.97
Na$_2$O	18.69
K$_2$O	0.05
ZnO	0.43
TiO$_2$	0.41
SO$_4$	3.20

Fig. 10. Spherical structure (cenosphere of the remaining fly ash) presented in the synthetic zeolitic material activated under 50 g SA-FA/1 L NaOH (at left: SEM photo-analysis 1 μm, at right: chemical composition of the spherical structure).
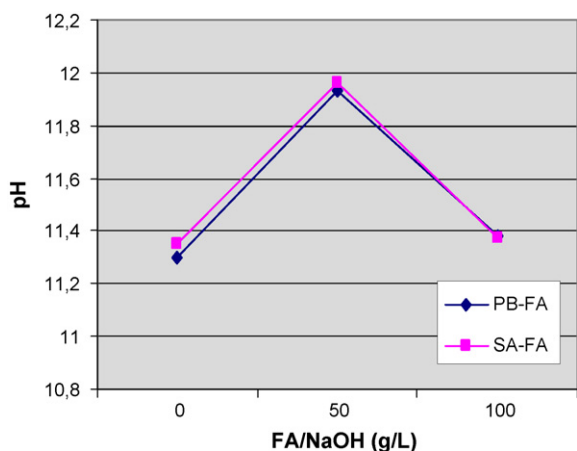
Fig. 11. pH evolution as a function of the treatment ratio of FAs.
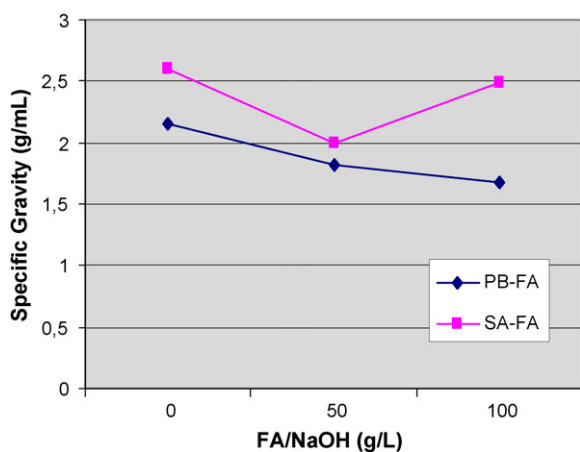

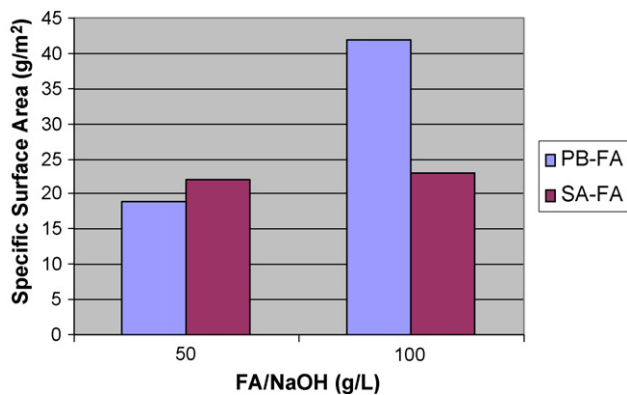**Fig. 12.** SG evolution as a function of the treatment ratio of FAs.

Fig. 13. SSA of the various synthetic zeolitic materials.

materials include a substantial range of porosity that can reach even the point of 37.5% of the total volume of the material. Actually, the range of porous structure in the synthesized zeolitic materials is, to a very important degree, greater in comparison to that of the normal respective amount in coal fly ashes. SA-FA treated with 100 g/L FA/NaOH ratio presents the most desired properties, concerning the remediation procedures for contaminants with bigger ionic radius, while PB-FA treated with 100 g/L FA/NaOH ratio can be easily applicable as smaller ionic retainer. Fig. 15 and illustrate the differences between the porous structures of the produced materials.

3.2. Removal of heavy metal using the synthetic zeolitic material

As expected, the synthetic zeolitic materials demonstrated a substantial ability to remove the pollutants from heavy metal-contaminated aqueous solutions. Indeed, none of the examined adsorbents presented removal percentages lower than 99.80%, which was the case for the removal of Cr by SA-FA product (50 g FA/1 M NaOH 1 M). On the contrary, on many occasions (Pb, Cd and Zn) the retaining percentages for both the types of zeolitic materials reached the point of 100%. It seems that the level of crystallization, and consequently the type of zeolites presented in the final hybrid materials, plays the most important role regarding their heavy metal-removing capacity. On the other hand, no sufficient general tendency was observed concerning the relation of the range of porosity and microporosity with the (%) removal
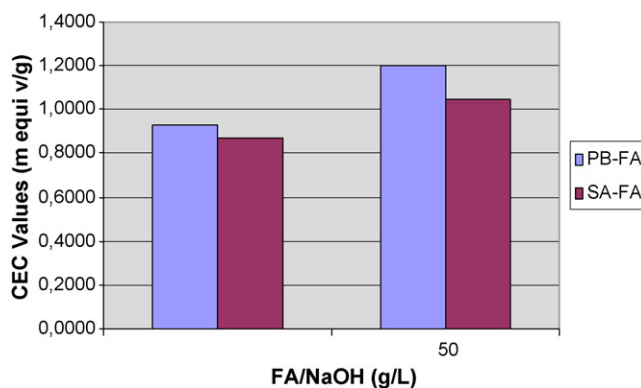

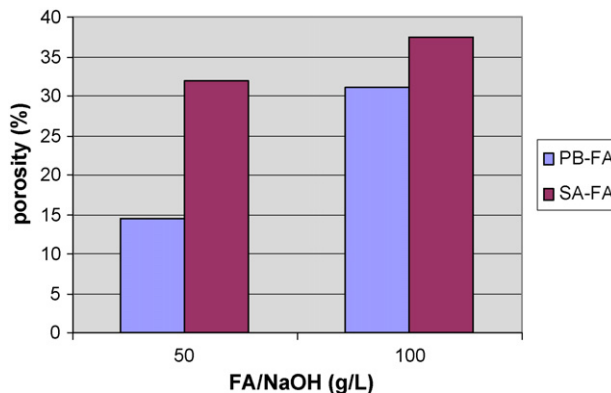**Fig. 14.** CEC values obtained from the various zeolitic materials.

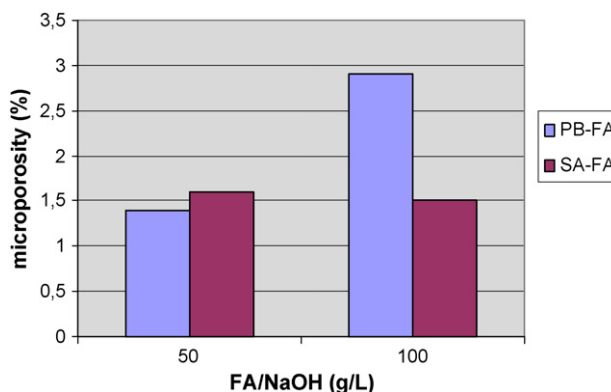**Fig. 15.** Porosity (%) of the various synthetic zeolitic materials.

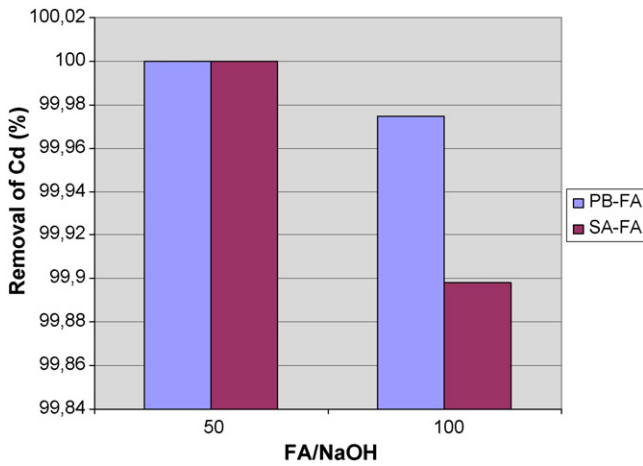**Fig. 16.** Micro-porosity (%) of the various synthetic zeolitic materials.

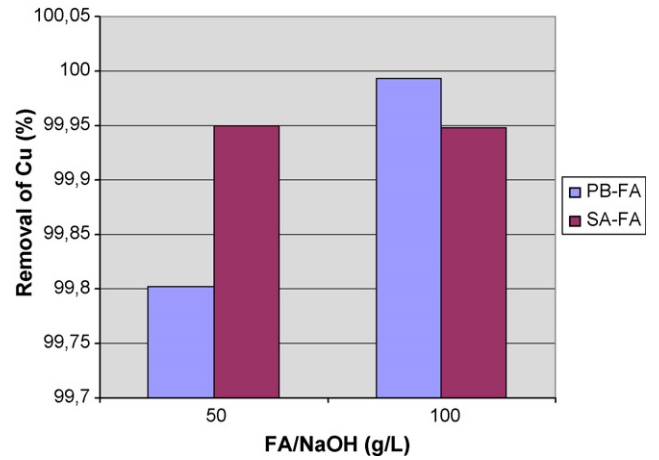**Fig. 17.** Removal (%) of Cd by the various synthetic zeolitic materials.
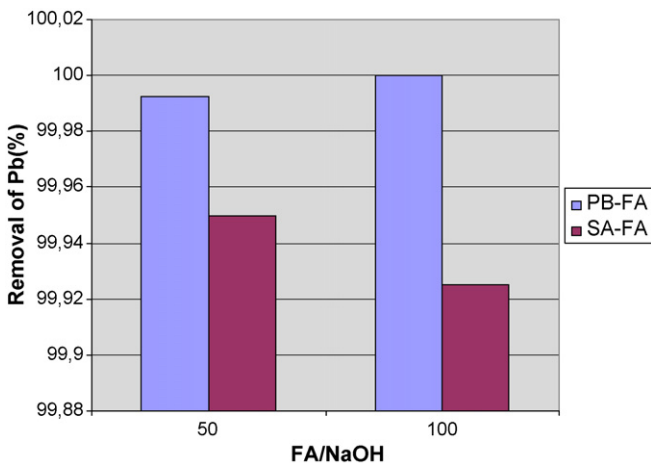

Fig. 18. Removal (%) of Pb by the various synthetic zeolitic materials.

Fig. 19. Removal (%) of Zn by the various synthetic zeolitic materials.

Fig. 20. Removal (%) of Cu by the various synthetic zeolitic materials.
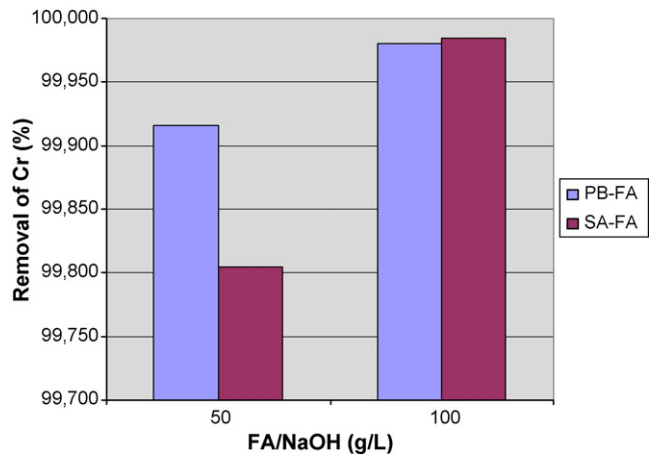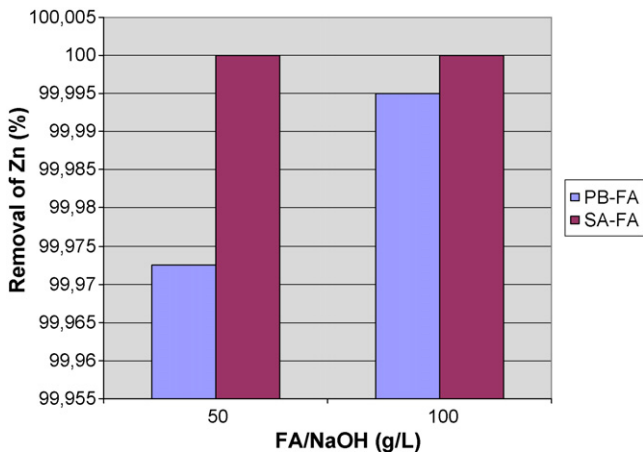

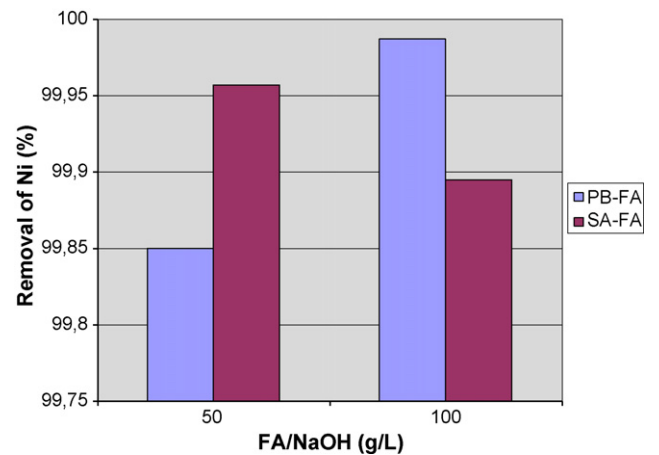**Fig. 21.** Removal (%) of Cr by the various synthetic zeolitic materials.

Fig. 22. Removal (%) of Ni by the various synthetic zeolitic materials.

of heavy metals. That fact can be attributed to the natural differences between the pollutants, thus driving the research to the separate study of each case of heavy metal. It should be mentioned that the percentages of removal are slightly increased in relation with that of the zeolite used as a supporter of biofilms [21–23] (Fig. 16).

Figs. 17–22 illustrate the ability of the synthetic materials to remove heavy metal from aqueous as a function of the ratio of the treatment of the FAs.

4. Conclusions

The chemical and mineralogical properties of two, CFB-derived, coal fly ashes render them suitable raw materials for the synthesis

of hybrid zeolitic materials. Keeping temperature, NaOH concentration and incubation time constant, the effect of FA/NaOH ratio on the zeolitic synthesis was investigated. The best treatment ratio for Polish bituminous fly ash is 100 g FA/1 L NaOH, for both the quantitative zeolite synthesis and the development of qualitative characteristics in the experimental products. Regarding the South African CFB-coal fly ash, both treatment ratios are equally effective for mono-mineral zeolite synthesis and for the required properties of the synthetic zeolitic materials in the field of the remediation of wastewaters. Cation exchange capacity, specific surface area and porous structure of the experimental products are improved in comparison to the initial of CFB-coal fly ashes. In addition, all the synthetic materials were tested for their ability to remove heavy metals from aqueous solutions and presented very encouraging results concerning their future, possible large-scale utilization.

Acknowledgments

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