

Comparative study on the characteristics of coal fly ash and biomass ash geopolymers

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Abstract: Geopolymers are a new class of materials that can be synthesized using natural minerals, and waste materials. Among these substrates, the use of fly ash is desirable as it involves the conversion of a copious waste material into a useful product. The aim of the research was geopolymers synthesis from coal fly ash and biomass ash. Concentrated sodium hydroxide and sodium silicate solutions were used as activators in geopolymerisation reaction. The results show that both coal fly ash and biomass ash can be utilized as source materials for the production of geopolymers. The surface morphology and chemical composition analysis were examined for the obtained geopolymers and ashes from coal and biomass combustion by SEM-EDS methods. It was found almost total disappearance of spherical forms of grains and reduction the porosity of structure for geopolymer based on fly ash from coal combustion. While the structure of the geopolymer based ash from biomass combustion is more porous. The UV-VIS-NIR spectra were performed on the coal fly ash, biomass ash and geopolymers. They showed that the obtained geopolymers possess optical and photocatalytic properties. The similarity of the geopolymer network and the zeolite framework in relation to ion exchange and accommodation of metal ions open questions on possibilities for the application of geopolymer materials as amorphous analogues of zeolite. The FT-IR spectra analyses were used on the geopolymers before and after metals sorption. It was found that geopolymer based on ash from biomass combustion has better sorption properties compared to geopolymer based on ash from coal combustion.

Introduction

In recent years, there has been remarkable technological progress in the development of materials known as geopolymers (Davidovits 2015). Geopolymers are amorphous materials, similar in construction to zeolites, yet having an amorphous structure. Hence, geopolymers can be described as amorphous analogs of zeolites (Sazama et al. 2011). Geopolymers indicate a lack of a long-range order and may have three basic structural units in a short range composed of: sialate $[-Si-O-Al-O-]_n$, siloxo-sialate $[-Si-O-Al-O-Si-O-]_n$, disiloxo-sialate $[-Si-O-Al-O-Si-O-Si-O-]_n$. Despite a similar structure, conditions to obtain geopolymers and zeolites are significantly different; in the case of the synthesis of zeolite A temperature up to 150°C and a pressure of 15 MPa are used, which allows to obtain individual crystals. In contrast, a temperature range of 20–80°C and atmospheric pressure (Davidovits 2015) are used for the synthesis of geopolymers.

Geopolymers have a number of unique properties, which makes them an interesting subject of research. These include, among others: fire resistance (Kong 2008), thermal resistance and acid resistance, high mechanical strength (Khan 2014). In addition, they reduce environmental pollution which results

from the application and production of materials associated with CO₂ emissions from cement kilns (McLellan et al. 2011). Also, they have low porosity, high water absorption and a lack of corrosion of steel reinforcement in the geopolymer (Mazur et al. 2013). In terms of environmental protection, the ability of geopolymers to immobilize heavy metals is important, which is related to their ability to ion exchange and a large surface development (Król et al. 2010). Metals such as cadmium, copper, lead, chromium, zinc and others may be immobilized in the geopolymer structure. However, too much amount of, e.g. zinc or chromium affects the decrease of compressive or bending strength (Zhang 2008).

Geopolymers are a new class of materials that can be synthesized using metakaolin, natural minerals and waste materials such as fly ash, slag, red mud or volcanic tuff (Faheem et al. 2013, He et al. 2012). Of all these materials, the use of ash from coal or biomass combustion is the most desirable as it is associated with the possibility of waste material conversion (i.e. a by-product of combustion) into a useful product (Böke et al. 2015). Geopolymers obtained from fly ash are a porous material, resistant to chemical corrosion and to low temperatures (Koukouzas et al. 2010). Also, the following substances are used for the synthesis of

geopolymers, respectively: bases, e.g. sodium or potassium hydroxide (Romisuhani 2015), sodium or potassium water glass or acids, however phosphoric acid is most often used for the activation of metakaolin. Acid-activated geopolymers constitute a relatively new group of materials with higher porosity, which suggests the possibility of using this group of geopolymers as adsorbents in the process of water purification. In contrast, alkali-activated geopolymers have been studied in many scientific papers due to their higher mechanical properties comparable to Portland cement (Zivica et al. 2014). It should be emphasized that the specific properties of a geopolymer are mostly determined by the aluminosilicate matrix, e.g. the structure of disiloxosialate is resistant to fire and corrosion, which results from the greater number of siloxane bonds compared to sialate (Khale and Chaudhary 2007).

The aim of the presented research was to demonstrate the synthesis of a geopolymer on the basis of coal fly ash and biomass ash and the indication of the possibility of their application. Concentrated NaOH and Na₂SiO₃ solutions were used as activators in the geopolymerization reaction. Surface morphology research and the analysis of chemical composition of the obtained geopolymers were performed using the SEM-EDS method. As part of the research, a comparison of the sorption and catalytic properties of geopolymers on the basis of coal fly ash and biomass ash was also made. For this purpose an experiment of sorption of the selected heavy metals (Cu, Mn, Pb and Zn) was performed and spectroscopic studies of the molecular structure of the obtained geopolymers before and after the sorption experiment using the FT-IR method were done. Also, spectra in the UV-VIS-NIR range were recorded. In addition, specific surface area measurements were made for the obtained geopolymers (BET isotherm and Langmuir isotherm) and the analysis of these isotherms for porous solids (t-Plot method and BJH method) was carried out.

Experimental

Materials

The ash from coal combustion was provided by the electric filter from a heat and power plant in Rzeszów, Poland. The ash from biomass combustion (wood chips of deciduous trees) was obtained in a heat and power plant in Arłamów, Poland. Chemical analysis of raw materials mentioned above was listed in Table 1 and their micrographs and results of EDS analysis are shown in Figs 1 and 2, respectively for ash from coal combustion and ash from biomass combustion. Alkaline solution was prepared by mixing sodium silicate with SiO₂/Na₂O = 2.4–2.6 molar module and 1.45–1.48 g/cm³ density (Chempur, Poland) with solid NaOH (analytical reagent grade, Chempur, Poland).

Geopolymers preparation

A solid mixture composed of 50 weight parts of sand and 50 weight parts of biomass ash or coal ash was prepared. Then, the mixture was dry blended for approx. 10 minutes on a laboratory shaker Vibramax 100, (Heidolph, Germany) to obtain a homogeneous mixture. Optimum molar module SiO₂/Na₂O of aqueous solution of sodium silicate equal to 1.28, which was obtained by mixing sodium silicate with solid NaOH in the ratio of 2:1 was used for the synthesis

of geopolymers. Then, a solid mixture (1:1) i.e., the ash with the addition of sand mixed thoroughly was added to the alkaline solution. It was prepared with a mixing time of 30 minutes. When a homogenous plastic consistency was obtained, the mixture was inserted into cylindrical moulds made from a plastic material (PE) with 14×30 mm dimensions. The samples were moulded by applying manual pressure, afterwards the samples were shaken for fifteen minutes on a laboratory shaker in order to release air bubbles. The samples were dried at room temperature under atmospheric pressure. After drying, the samples were removed from the moulds. To avoid errors during the analyses, three control samples were prepared, eliminating the possibility of accidental phenomena influencing end results.

Sorption experiments

In order to determine sorption properties, the obtained geopolymers were treated with an aqueous solution of 0.01 M NH₄NO₃ to remove unreacted Na⁺ ions from their structure, and then with solutions of corresponding metal salts: ZnCl₂, MnCl₂, CuCl₂, Pb(NO₃)₂ with a concentration of 0.01 mol/dm³. For this purpose, 1.00 g of powdered geopolymer sample was added to 100 cm³ of 0.01 M NH₄NO₃ and was shaken thoroughly for 24 hours on Vibramax 100 laboratory shaker (v = 300 rpm). After this time, the separation phase was started by centrifugation (t = 5 min, v = 2000 rpm) and the obtained precipitates were dried at ambient temperature. 100 cm³ of solutions of the corresponding metal salts: ZnCl₂, MnCl₂, CuCl₂, Pb(NO₃)₂ with an initial concentration of 0.01 mol/dm³ was added to the obtained samples and they were then shaken thoroughly for 24 hours under conditions described above. Further procedure was analogous, in the obtained solutions the content of Zn, Mn, Cu and Pb was determined by the FAAS method – a detailed description was included in a paper by Kalembkiewicz 2015. All experiments were performed without correction of the pH value of solutions.

Desorption experiments

The stability of the bonds between the metal ions and the geopolymers, respectively of ash from coal or biomass combustion was established on the basis of the experiment of desorption. For this purpose, to the samples after sorption was added 100 cm³ of solution 1 M ammonium acetate, pH = 7.00, which removes metal ions with ion-exchange position. Then the samples were shaken and in the obtained solutions the content of Zn, Mn, Cu and Pb was determined by the FAAS method – a detailed description was included in the sorption experiment (2.3.).

Materials and geopolymers characterization

Scanning electron microscope SEM (Hitachi S-3400N) equipped with an energy-dispersive X-ray spectroscopy detector (EDS) was employed to determine the microstructure and chemical composition of the ashes and geopolymer samples. Preparations were made by placing the samples on a carbon belt with gold sputtering.

The UV-VIS-NIR diffuse-reflectance spectra of ashes and geopolymers were recorded using a Jasco V-670 spectrometer. They were registered in the range of 250–2500 nm, at room temperature, using BaSO₄ as a reference.

The infrared spectra of absorption were recorded at the basic level from 4000–400 cm^{-1} with a resolution of 2 cm^{-1} with Bruker (Germany) FTIR ALPHA spectrometer. Powder preparations for the analysis were made by mixing approx. 0.5 mg of the analyzed sample with 200 mg of spectrally pure KBr. A product in the form of a pill was formed after putting the prepared mixture in vacuum at a pressure of 10 MPa.

Nitrogen sorption isotherms of geopolymers were measured with ASAP 2420 (Micromeritics Instrument Corporation, Norcross, USA) apparatus, at a temperature of 196 °C. Prior to the sorption measurements, all of the samples were degassed at 120°C for at least 24 hours at a pressure of 10^{-3} Pa.

Chemical analyses (for Cu, Mn, Pb and Zn) in the aqueous solutions obtained from the adsorption tests were performed using flame atomic absorption spectrometer Perkin-Elmer 3100 Model (Shelton Instruments, CT USA).

Results and discussion

Research of morphology of surface and the analysis of chemical composition

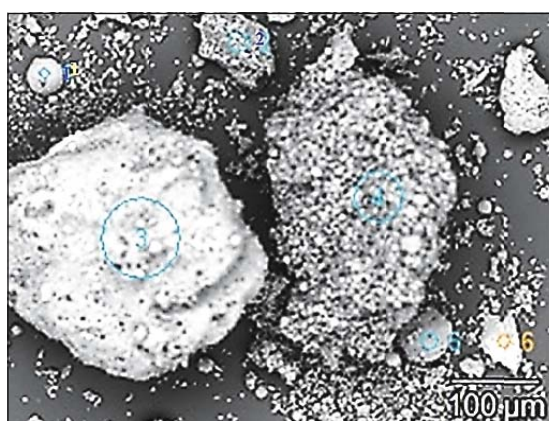
Energy-dispersive X-ray spectroscopy (EDS) in combination with scanning electron microscopy (SEM) was used to demonstrate the elemental composition of geopolymers.

Changes in the microstructure in raw ash samples were presented in Figs 1a and 2a, whereas Figs 3a and 4a show changes in the obtained geopolymers. Microscopic analysis leads to the conclusion that the fly ash from coal combustion is dominated by silicate and aluminosilicate spherical forms of very diverse sizes (from 2 μm to 45 μm) and their aggregates are noticeable. Based on the analysis of SEM image of biomass ash (Fig. 2a), it was found that the diameters of the particles have different sizes, but not exceed 250 μm . The ash is fine-grained, has an amorphous structure with aggregates.

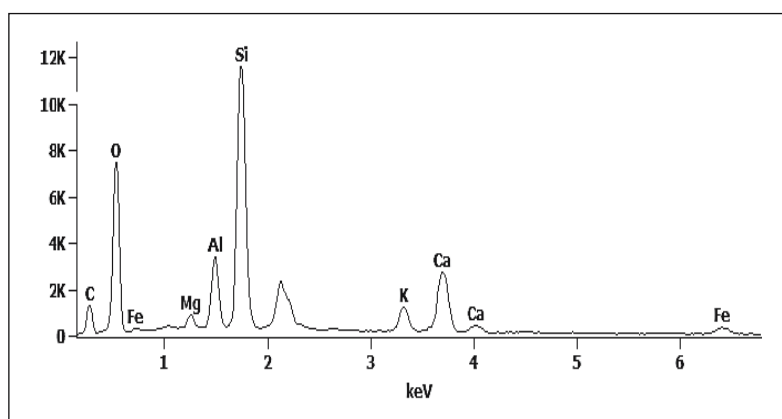
Surfaces of all geopolymers are heterogeneous, which is typical for fly ash-based geopolymers.

As shown in Figure 3a, geopolymers synthesized from coal ash are mainly composed of the whole ash particles, on the surface of which exist insoluble Si, Al compounds and other surface impurities (Sindhunata et al. 2006). Biomass ash-based geopolymers indicated a high degree of geopolymerization (Fig. 4a), however some unreacted ash particles were also found. The SEM image of geopolymer (Fig. 4a) showed that as a result of geopolymerization, structure becomes more porous and open in comparison to biomass ash. In the structure dominated aluminosilicates with size larger than 200 μm .

As regards both geopolymers, it was shown that geopolymerization was not complete, which is common for geopolymers on the basis of complex waste materials, such

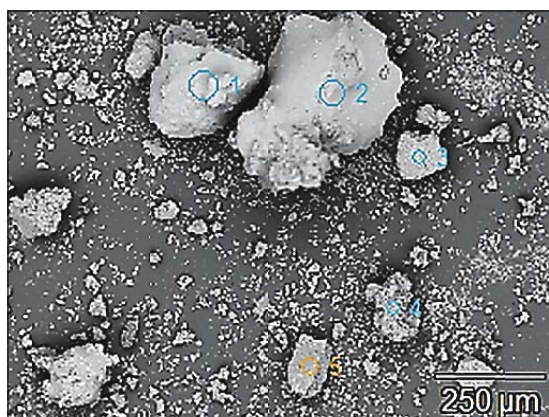


a. SEM image of coal ash

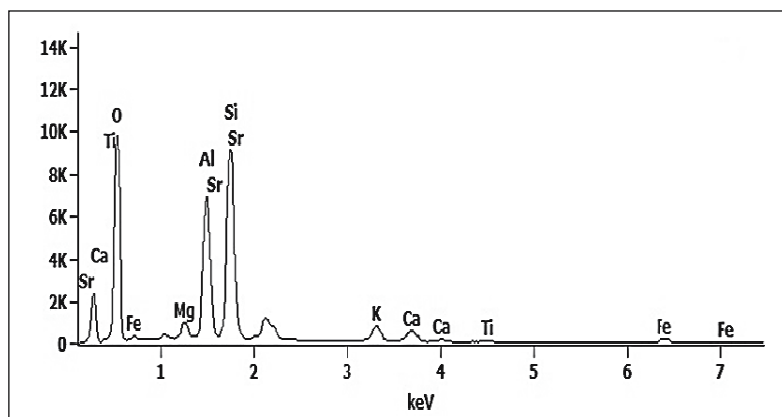


b. EDS analysis of coal ash

Fig. 1. SEM/EDS analysis of coal ash



a. SEM image of biomass ash



b. EDS analysis of biomass ash

Fig. 2. SEM/EDS analysis of biomass ash

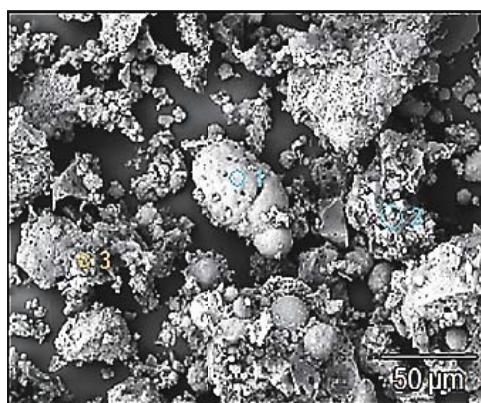
as fly ash (Zhang et al. 2012). The reason for this may be the fact that as a result of condensation reaction, the newly formed aluminosilicate gel covers the surface of ash particles preventing the release of Si and Al from the surface, thereby suppressing further geopolymerization reaction (Murayama et al. 2002). When the geopolymerization reaction is not entirely complete, an excess of Na⁺ ions appears on the geopolymer surface in the form of salts (Delair et al. 2012). They are visible for both geopolymers in Figs 3a and 4a.

The grains mainly consist of sodium according to the EDS analysis, the results of which are presented in Table 1. As determined by EDS, the predominant elements in the fly ash and biomass ash samples (Figs 1a and 2a) were silicon, aluminum, iron, calcium, manganese and oxygen in various compounds. Aluminum was primarily associated with silicon.

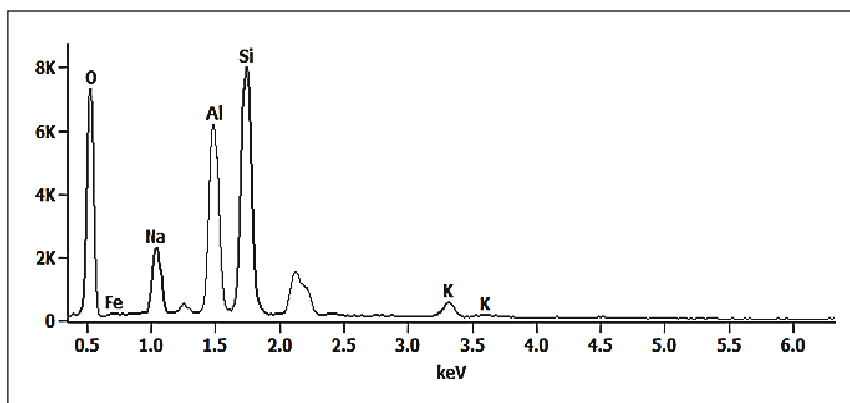
The chemical analysis of coal ash-based geopolymers in the points visible in Figure 3a showed that O, Na, Si and Al are the main elements of geopolymers. In addition, there are also minor impurities, such as Fe, K and Mg originating from ashes from coal combustion. In contrast, chemical analysis of biomass ash based geopolymers in the points visible in Fig. 4a showed the presence of: O, Na, Si and Al, which are the main elements forming these geopolymers, there are also minor impurities such as K and Ca resulting from biomass combustion ashes.

Chemical structure of geopolymers

An important feature of the obtained geopolymers as adsorbents is the chemical nature of their surface. It affects the sorption capacity of the adsorbents and determines the type of interactions between the adsorbate and the adsorbent. The chemical nature of the sorbents surface results directly from the number and

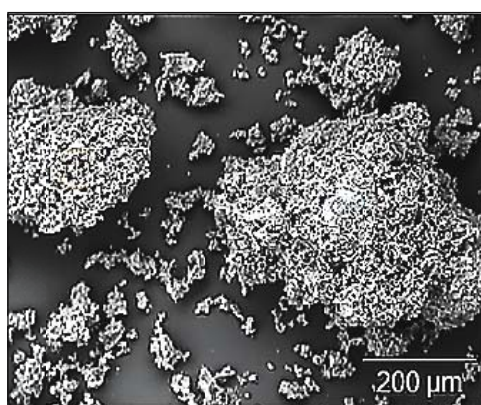


a. SEM image of geopolymer PW/GEO

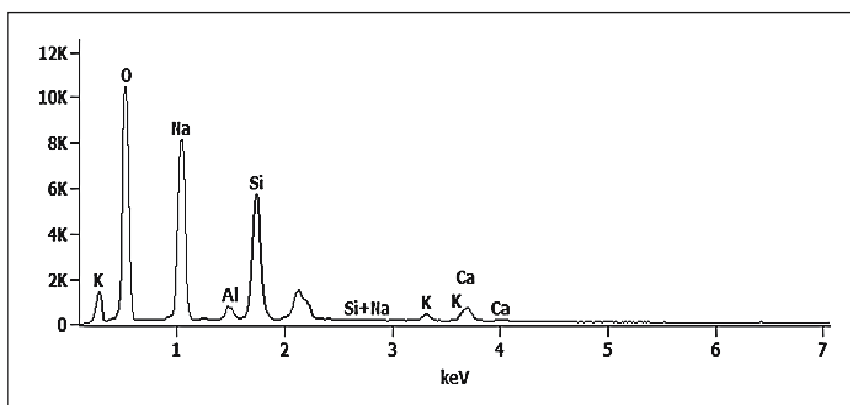


b. EDS analysis of geopolymer PW/GEO

Fig. 3. SEM/EDS analysis of geopolymer PW/GEO



a. SEM image of geopolymer PB/GEO



b. EDS analysis of geopolymer PB/GEO

Fig. 4. SEM/EDS analysis of geopolymer PB/GEO

Table 1. The composition of the mineral phase of ash and geopolymers samples determined by EDS analysis

Type of samples	Content [% weight]						
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	Fe ₂ O ₃	CaO
Coal ash	2.45	3.73	25.32	45.64	3.3	5.7	5.23
PW/GEO	51.65	0.53	9.41	16.81	6.49	1.20	–
Biomass ash	–	1.56	5.16	17.5	17.22	1.48	10.99
PB/GEO	51.60	–	1.09	16.88	2.46	–	3.63

the type of functional groups on the surface of the sorbent. The most common groups include oxygen functional groups, e.g. hydroxyl, carboxyl, carbonyl (Bożęcka et al. 2014).

In order to determine the chemical structure of the obtained geopolymers, the FT-IR method was used. Based on the spectra recorded for geopolymers obtained from ash from coal combustion (PW/GEO) and ash from biomass combustion (PB/GEO), identification of functional groups presented on the surface of geopolymers was made (Fig. 5).

A band visible on a spectrum (Fig. 5) in the range of 3500–3200 cm^{-1} with the maximum adsorption at approx. 3440 cm^{-1} is attributed to vibrations stretching -OH group. It may result from -OH group chemically bound with ash surface, as well as from vibrations stretching the H-O-H, i.e. water molecules adsorbed on the surface of the ash. The most intense band is located at approx. 1060 cm^{-1} . It can be attributed to vibrations Si-O(Al) and Si-O(Si). (Król et al. 2018). In addition, by comparing the coal ash-based geopolymer (PW/GEO) with biomass ash-based geopolymer (PB/GEO), it was found that all of the abovementioned bands show greater intensity for the PB/GEO. For this geopolymer at band of approx. 1060 cm^{-1} (corresponding to vibrations from the geopolymer structure, i.e. the internal vibrations Si-O(Al) and Si-O(Si)), the overlapping second band at a wavenumber of approx. 970 cm^{-1} is visible, which corresponds to symmetric or asymmetric vibrations of Si(Al)-O bonds. From the spectra analysis it appears that the PB/GEO, in comparison to the PW/GEO, demonstrates a large half-width of the abovementioned bands, which is a result of a structure disorder of biomass ash-based geopolymer and indicates its amorphousness. The results of FTIR spectra analysis of obtained geopolymers confirm the results obtained by other authors, e.g. (Liu et al. 2016, Bakharew 2005).

In sum, the investigated geopolymers have a complex chemical structure. Among the surface functional groups, the following groups (being the “active sites” of adsorbents) are predominant: hydroxyl and carbonyl. The affinity of the abovementioned functional groups to the selected metal ions can be ranked as follows (Oliveira et al. 2008):

- carboxyl: Zn(II) > Cu(II) > Cr(VI) > Cd(II),
- alkaline: Cu(II) > Cr(VI) > Cd(II) > Zn(II),
- phenolic: Cr(VI) > Zn(II) > Cd(II) > Cu(II),
- lactone: Cr(VI) > Zn(II) > Cd(II) > Cu(II).

Catalytic properties of geopolymers

Catalytic properties of the obtained geopolymers were determined on the basis of the analysis of UV-VIS-NIR spectra.

They are presented in Fig. 6a – PW/GEO and Fig. 6b – PB/GEO. There are visible vibrations resulting from aluminium-silicon skeleton (~ 1500 and 2000 nm) on the spectra. The presence of a peak at around 1500 nm in the NIR range means that the obtained geopolymers are transparent to visible light. Owing to this, a broad opportunity is opening up to the use of geopolymers for optical and photocatalytic applications (Karamanis and Vardoulakis 2012).

The comparison of values of reflectance coefficients for particular radiation ranges, i.e. UV 280–400 nm, VIS 400–700 nm and NIR 700–2500 nm are presented in Table 2. For both of the obtained geopolymers, the values of reflectance are exceeded by 60% indicating their potential application as active photocatalysts in the range of visible light. The value of reflectance for the obtained geopolymers in all ranges of radiation is higher compared to the starting materials, i.e. ashes, whereas the highest values of this parameter are shown for the PW/GEO geopolymer. It is possible to indicate the potential use of the obtained coal ash-based geopolymer as a cheap and effective photocatalyst, active in a visible spectrum. It should be emphasized that photocatalytic degradation processes are a very promising method of removing environmental pollution due to low costs, mild conditions of the process (temperature, pressure) and the possibility of total mineralization of pollutants (Yu et al. 2012).

Sorption properties of geopolymers

Metal ions in aqueous solutions exist in various forms, which may adsorb on the surface of the adsorbent or precipitate on its surface. In acidic and weakly acidic solutions, the investigated metals occur primarily in the form of Me^{2+} straight ions. As such, they can react with hydroxyl and carbonyl groups of adsorbents according to the following equations (El-Shafey 2010):

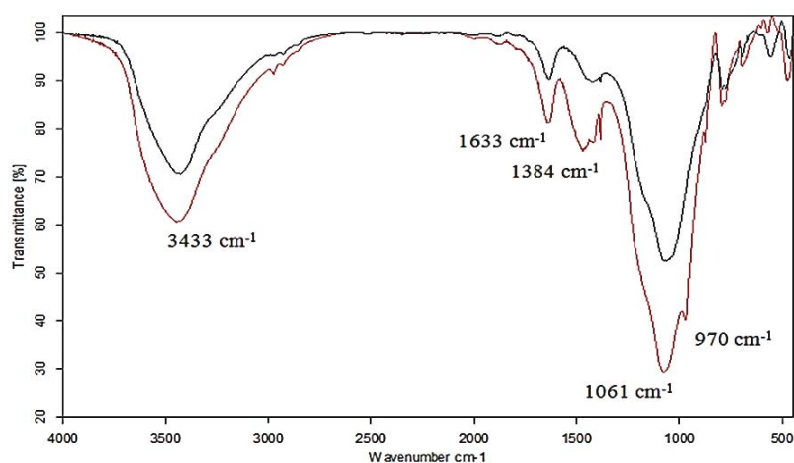
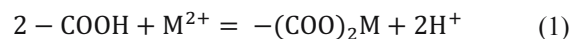


Fig. 5. FT-IR spectra of geopolymers; PW/GEO – color black and PB/GEO – color red

Carbonyl groups, i.e. active sites, are not protonated in alkaline solutions, which allows for the adsorption of positively charged ions of metal (O'Connell et al. 2008). Due to the fact that the concentration of ions $[H^+]$ in the solution decreases (functional groups are deprotonated) with the unchanged concentration of metal ions, the amount of the adsorbed metal increases.

In order to compare sorption properties of coal ash and biomass ash-based geopolymers, FT-IR spectra after sorption of Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} ions from mono-component aqueous solutions with a concentration of 0.01 mol/dm^3 were recorded. They are presented in Figure 7.

There are intense bands in 3 different ranges in the infrared spectra (Fig. 7a):

- bands in the range of $3600\text{--}3200 \text{ cm}^{-1}$ connected with vibrations stretching OH groups,
- bands in the range $1760\text{--}1630 \text{ cm}^{-1}$ connected with vibrations stretching C=O bond, as
- bands in the range $1200\text{--}450 \text{ cm}^{-1}$ range, i.e. internal vibrations Si-O(Si) and Si-O(Al) in tetrahedral oxygen bridges, asymmetric or symmetric bending vibration Si(Al)-O.

All the bands described above have higher intensity for the biomass ash-based geopolymer (PB/GEO) after the Zn^{2+} ions sorption process. This confirms structural differences in the investigated geopolymers. The remaining bands do not have any diagnostic significance due to their low intensity.

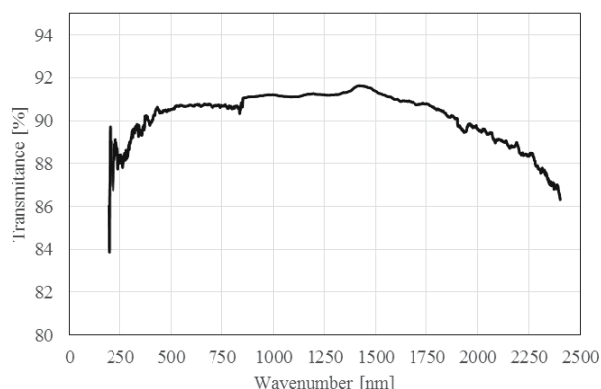
After sorption of Mn^{2+} and Cu^{2+} ions (Figs 7b and 7c) the spectra indicate analogous bands of adsorption, the same as geopolymer samples after Zn^{2+} ion sorption. There are visible bands on the spectra at a wavenumber of approximately 3430 cm^{-1} from -OH. The highest intensity has a band at a wavenumber of approximately 1040 cm^{-1} from structural vibrations of geopolymers. The band at approx. 1630 cm^{-1}

indicates the vibrations stretching C=O bond (Rożek et al. 2018). The analyzed bands have greater intensity for PB/GEO. Spectrograms of the investigated geopolymers after Pb^{2+} ion sorption (Fig. 7d) are different from the spectra after sorption of the remaining investigated ions of heavy metal, which results from the presence of a much more intense band in the range of $1500\text{--}1400 \text{ cm}^{-1}$. In general, there are changes in three ranges on the spectra, analogous as in Figure 7a. In addition, in the range of $1500\text{--}1400 \text{ cm}^{-1}$ are bands connected with vibrations stretching C-O.

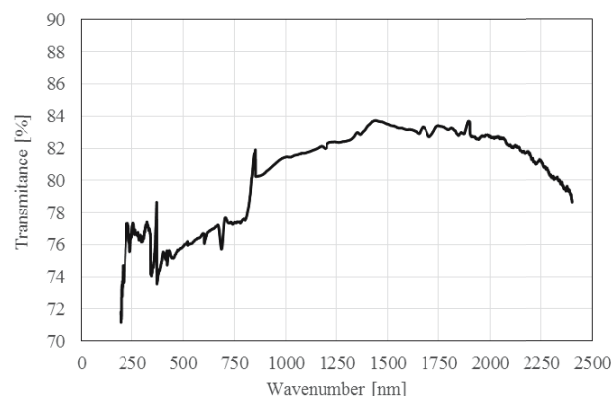
The new band at a wavenumber of approximately 1420 cm^{-1} results from vibrations stretching C-O groups, which are shared in a large degree in the sorption of metal ions. It may confirm the fact that the adsorption of Pb^{2+} ions by the investigated geopolymers was the highest. The remaining bands have an analogous course like after the sorption process of Cu^{2+} , Zn^{2+} , Mn^{2+} ions, and most importantly, the interpreted bands show greater intensity for the PB/GEO.

It should be emphasized that on each recorded spectrum after sorption of the investigated ions, the presence of a band at 675 cm^{-1} was found, which is associated with the sorption of heavy metals, therefore it can be treated as an indicator of the sorption process (Mozgawa et al. 2009). Its presence demonstrates the ion exchange process and leads to changes in charge and ionic radiation of cations and a deformation of the structure of a geopolymer.

In sum, the largest changes in the registered FT-IR spectra for the PB/GEO are observed for Zn^{2+} ions, in the area corresponding to vibration C=O of carbonyl group (about 1560 cm^{-1}) the band after adsorption of Zn^{2+} ions is moved to lower wavenumbers. The formation of a bond between Zn^{2+} ion and the carbonyl/carboxyl group causes elongation of C-O bond and the reduction of their constant force, and



a. UV-VIS-NIR spectra of geopolymers PW/GEO



b. UV-VIS-NIR spectra of geopolymers PB/GEO

Fig. 6. UV-VIS-NIR spectra of geopolymers a) PW/GEO and b) PB/GEO

Table 2. The summary of the reflection coefficients

Type of samples	SRUV (%)	SRVIS (%)	SRNIR (%)
Coal asah	68	72	72
PW/GEO	89	90	91
Biomass ash	65	68	74
PB/GEO	75	76	84

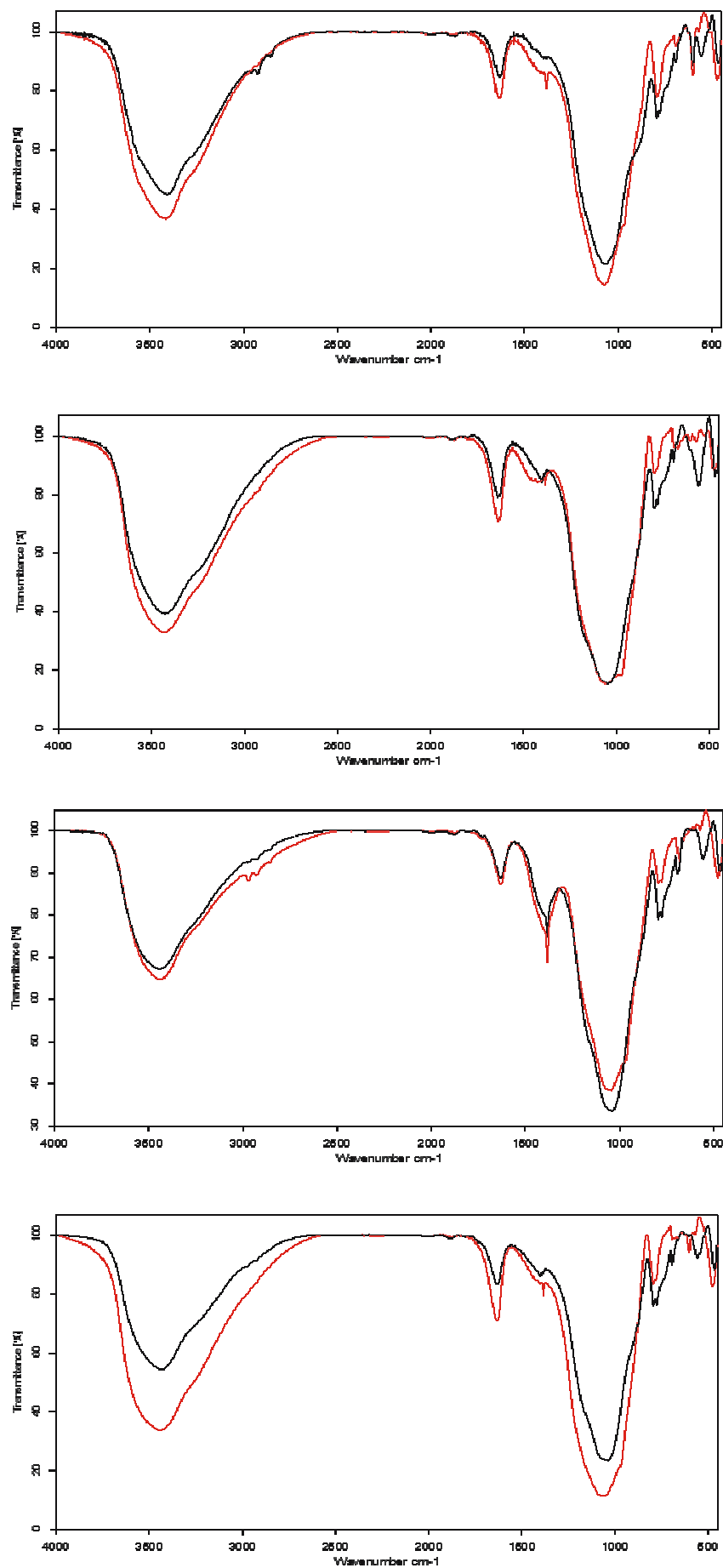


Fig. 7. FT-IR spectra after sorption the tested ions: a) Zn^{2+} , b) Mn^{2+} , c) Cu^{2+} , d) Pb^{2+} for initial metal concentration 0.01 mol/dm^3 by geopolymers PB/GEO (line red) and PW/GEO (line black)

consequently, C=O band moves in the direction of a smaller wavenumber values. Whereas, for the PW/GEO, there is a significant reduction in the intensity of the band at approx. 1420 cm^{-1} resulting from C-O vibrations.

This indicates the chemical binding of ions to the investigated sorbents (PW/GEO and PB/GEO), i.e. chemisorption. Investigated cations of metals are “soft cations”, which means that they bind to the oxygen from functional groups (-COO, -CO, -OH, as previously identified) much weaker, thereby deforming the geopolymer structure slightly. The bands associated with these cations are found in far infrared, e.g. for Zn^{2+} $246\text{--}228\text{ cm}^{-1}$, Mn^{2+} 320 cm^{-1} (Roa and Euiott 1981), hence they were not registered on the FT-IR spectra.

Mechanism of metal sorption

One of the most important application areas for sorbents is their use in the immobilization of heavy metals. Such immobilization of cations causes their permanent deactivation and makes them harmless (Bailey et al. 1999). The immobilization of heavy metal ions in the structure of a geopolymer may occur as a result of a physical encapsulation by adsorption of metal ions into the structure of a geopolymer or the possibility of incorporating metal ions into the structure of a geopolymer (Khale and Chaudhary 2007).

Heavy metal cations may be immobilized on sorbents by two mechanisms, i.e. ion exchange and chemisorption. Figures 8a and 8b show the participation of both sorption mechanisms for coal ash and biomass ash-based geopolymers in relation to the following metal cations: Cu^{2+} , Pb^{2+} , Mn^{2+} , Zn^{2+} using a solution of each metal with an initial concentration equal to 0.01 mol/dm^3 .

The sorption mechanism comprising ion exchange and chemisorption was determined on the basis of the result of spectroscopic studies (FTIR). The quantitative part of both processes was estimated based on the results of atomic absorption spectrometry (FAAS). Ion exchange is a reversible process the result of which is the formation of poor bonds between the geopolymer and metal ions (van der Waals bonds). The ion exchange process was quantitatively estimated based

on the results of the sorption and desorption experiment. The difference between the concentration of metal after sorption and desorption is the share of chemisorption.

The proportion of chemisorption is comparable to ion exchange for the two tested geopolymers PW/GEO and PB/GEO. In reference to particular ions of the investigated metals it amounts to Cu^{2+} – 123.5, Mn^{2+} – 108, Pb^{2+} – 401, Zn^{2+} – 127 mg/g. In turn, for a biomass ash geopolymer, the proportion of chemisorption is equal to Cu^{2+} – 124, Mn^{2+} – 110, Pb^{2+} – 408, Zn^{2+} – 127 mg/g. The available literature data indicate that fly ash-based geopolymer materials have better immobilization properties of heavy metals than sorbents based on untreated ashes (Al-Zboona et al. 2011). The obtained results are consistent with the quoted literature data. The sorption processes of the investigated ions i.e. Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} on the obtained geopolymers from the biomass and coal combustion are carried out according to the ion exchange mechanism and chemisorption.

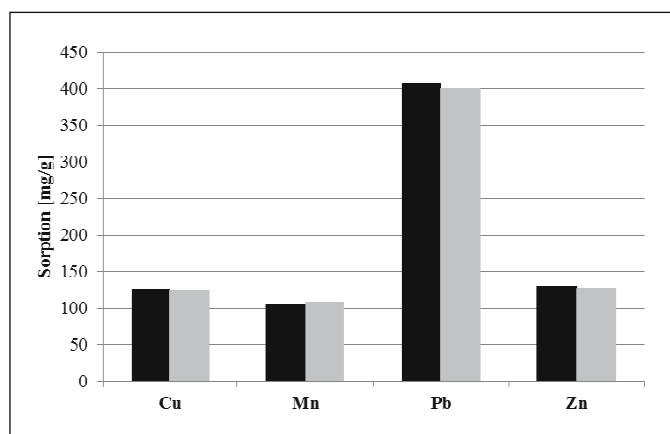
The sorption capacities of the obtained geopolymers were compared based on the value of the adsorption coefficient for individual metals. It is an average of 3 measurements of metal content in the solution determined by the FAAS method. The total efficiency of the adsorption process of the investigated heavy metal ions is the same for individual cations, regardless of a geopolymer used. The following values of the adsorption coefficient were obtained for individual ions:

- for PW/GEO respectively: Cu^{2+} – 97, Mn^{2+} and Pb^{2+} – 96, Zn^{2+} – 93%;
- for PB/GEO respectively: Cu^{2+} – 97, Mn^{2+} and Pb^{2+} – 96, Zn^{2+} – 93%.

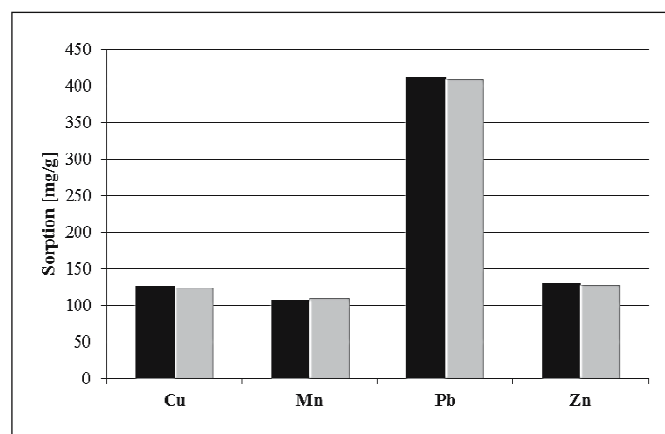
It was found that the effectiveness of adsorption process does not depend on the geopolymers used and its value is the same for each metal ions.

Isotherm of sorption

The porosimetric research results are shown in Table 3. The values of a specific surface area, volume and pore size for the obtained geopolymers are presented. By comparing both of the geopolymers in terms of the obtained BET surface areas



a. Participation of sorption mechanisms on the PW/GEO for the tested ions for initial metal concentration 0.01 mol/dm^3 (color black – ion exchange, color grey – chemisorption)



b. Participation of sorption mechanisms on the PB/GEO for the tested ions for initial metal concentration 0.01 mol/dm^3 (color black – ion exchange, color grey – chemisorption)

Fig. 8. Participation of sorption mechanisms on the a) PB/GEO and b) PW/GEO for the tested ions for initial metal concentration 0.01 mol/dm^3 (color black – ion exchange, color grey – chemisorption)

Table 3. Structure parameters of porous structure of geopolymers designated on the basis of low-temperature adsorption and desorption of nitrogen

	PW/GEO	PB/GEO
Surface area [m²/g]		
Single point surface area at $P/P_0 = 0.249$	3.02	3.30
BET Surface Area	3.15	3.45
Langmuir Surface Area	4.45	4.91
t-Plot External Surface Area	3.20	3.52
Pore volume [cm³/g]		
Single point desorption total pore volume of pores less than 805.413 Å diameter at $P/P_0 = 0.975$	0.0174	0.0183
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.0185	0.0188
BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.0189	0.0192
Pore size [Å]		
Desorption average pore width (4V/A by BET)	221.79	211.75
BJH Adsorption average pore diameter (4V/A)	257.45	229.38
BJH Desorption average pore diameter (4V/A)	141.32	123.73

it was found that the PW/GEO has a smaller value of BET surface area, equal to 3.15 m²/g and 3.45 m²/g for the PB/GEO. The total micropores area determined by the t-method for the PW/GEO is equal to 3.2 m²/g, while it is 3.52 m²/g for the PB/GEO, which in both cases constitutes about 100% of the specific surface area.

Conclusion

Conventional methods of removing toxic metals from water and wastewater (e.g. ion exchange, chemical precipitation, adsorption on activated carbons, zeolites, coagulation, flocculation, evaporation, ultra or nanofiltration, electrochemical methods) have a number of disadvantages and limitations. Therefore, new sorbents which have a high efficiency of removing heavy metal ions from aqueous solutions are sought. These include geopolymers, among others. Geopolymers obtained from fly ash are a porous material, resistant to chemical corrosion and to low temperatures. The available literature data indicate that fly ash-based geopolymer materials have better immobilization properties of heavy metals than sorbents based on untreated ashes. The obtained results are consistent with the quoted literature data. The sorption processes of the investigated ions i.e. Cu²⁺, Mn²⁺, Pb²⁺ and Zn²⁺ on the obtained geopolymers from the biomass and coal combustion are carried out according to the ion exchange mechanism and chemisorption. On the basis of the obtained results, it seems appropriate and justified to use the obtained geopolymers in the immobilization of Cu²⁺, Mn²⁺, Pb²⁺ and Zn²⁺ ions, due to the fact that it causes their deactivation and makes them harmless.

It should be emphasized that the production of geopolymers based on ashes from the coal and biomass combustion is a new way of management of this waste from energy industry, in addition, it allows reducing their negative influence on natural environment. The obtained geopolymers have very good

surface-sorption and catalytic properties, which will be the subject of further research.

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Porównanie właściwości geopolimerów na bazie lotnego popiołu ze spalania węgla i biomasy

Streszczenie: Geopolimery są nową klasą materiałów, które mogą być syntetyzowane z użyciem naturalnych minerałów i materiałów odpadowych. Wśród tych substratów, użycie popiołu lotnego jest pożądane ponieważ wiąże się z możliwością konwersji materiału odpadowego w użyteczny produkt. Celem badań była synteza geopolimerów z lotnego popiołu węglowego oraz z popiołu z biomasy. Jako aktywatory reakcji geopolimeryzacji były stosowane stężony wodorotlenek sodu i roztwór krzemianu sodu. Rezultaty pokazują, że zarówno lotny popiół węglowy i popiół z biomasy mogą być wykorzystane jako źródło materiałów do produkcji geopolimerów. Badania morfologii powierzchni i analizę składu chemicznego dla otrzymanych geopolimerów i popiołów ze spalania węgla i biomasy wykonano metodą SEM-EDS. Stwierdzono prawie całkowity zanik form kulistych ziaren i zmniejszenie porowatości struktury dla geopolimeru na bazie popiołu lotnego ze spalania węgla. W przypadku geopolimeru na bazie popiołu ze spalania biomasy występuje struktura bardziej porowata. Widma UV-VIS zostały wykonane dla lotnego popiołu węglowego, popiołu z biomasy oraz geopolimerów. Pokazują one, że otrzymane geopolimery wykazują właściwości optyczne i fotokatalityczne. Podobieństwo sieci geopolimeru i struktury zeolitu w związku z wymianą jonową i akomodacją jonów metali otwiera pytania dotyczące możliwości zastosowania materiałów geopolimerowych, jako bezpostaciowych analogów zeolitu. Widma FT-IR zostały wykonane dla geopolimerów przed i po sorpcji metali. Stwierdzono, że geopolimer na bazie popiołu z biomasy ma lepsze właściwości sorpcyjne w porównaniu do geopolimeru na bazie popiołu lotnego ze spalania węgla.