

# Synthesis of geopolymers on fly ash from biomass combustion

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**Abstract** Fly ash from biomass combustion aren't used in numerous economic branches. Their increased production make it necessary for researches to look for synthesis new products. The chemical composition of fly ash from biomass combustion are similar to those of fly ash from coal, they can be used as raw material for geopolymer synthesis.

The aim of the research was to assess feasibility of geopolymer synthesis from fly ash from biomass by geopolymerisation method. The effect of temperature, curing time and the ratio of fly ash to alkaline activator (sodium hydroxide and sodium water glass) impact in the formability of geopolymers mass were investigated.

On the basic of the research investigations, optimal conditions of geopolymerisation have been determined. We have also found, that optimal conditions for synthesis of geopolymers on fly ash from biomass combustion are following: temperature – 20 °C, curing time 17 hours and the ratio of fly ash [g] to alkaline activator [cm<sup>3</sup>] – 50:50. The surface morphology and chemical composition analysis (before and after geopolymerisation) were examined for the obtained geopolymers by SEM-EDS methods. The UV-VIS-NIR spectra (before and after geopolymerisation) were performed. They showed, that received geopolymers possess optical and photocatalytic properties.

**Keywords:** biomass ash, geopolymer, waste utilization

## 1. Introduction

One of the most important sources of renewable energy in the power industry is biomass. Combustion of biomass (similarly to the conventional fuel) causes the formation of solid combustion by-products [Vassilev *et al.*, 2010, 2013a]. It is estimated that about 480 million tons of ash from combustion and co-combustion of biomass can be generated every year in the world, with the assumption that the amount combusted biomass is 7 billion tons per year [Vassilev *et al.*, 2010, 2012, 2013a]. Application of waste from combustion and co-combustion of biomass is related to their physicochemical properties, which in turn depend primarily on the type of biomass and combustion technology [Girón *et al.*, 2013; Kalemekiewicz and Chmielarz, 2012]. Fly ashes constitute large part of the waste from the combustion of biomass, they have variable chemical and phase composition, whereby are difficult to management [Rajamma *et al.*, 2009]. Nevertheless, it is

possible to identify potential areas of their application, eg. in agriculture and forestry, as fertilizer or anti-acidification substance of soils [Aronsson and Ekelund, 2004; Brunner *et al.*, 2004; Kuba *et al.*, 2008], construction and industrial purposes. A comprehensive overview of potential technological applications of ashes from the combustion of biomass are presented in the work Vassilev *et al.*, 2013b. They include, among others, production of concrete, cement and road construction [Rajamma *et al.*, 2009; James *et al.*, 2012]. The use of ash from biomass as building materials is recommended by the EU (European Directive on waste 2008/98/CE) due to CO<sub>2</sub> emissions and reduction of accumulated waste [Melotti *et al.*, 2013]. The possibility of application of ash from biomass as raw material for the preparation of geopolymers were analyzed in several works [Songpiriyakij *et al.*, 2010; Novais *et al.*, 2016a-e, Novais *et al.*, 2017, Murri *et al.*, 2015].

In general, geopolymers are three-dimensional, amorphous-to-semi-crystalline aluminosilicate materials [Davidovits, 1998]. They are composed of successive SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra connected through an oxygen-bridged bonding framework, in which positive ions (Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup> or Ca<sup>2+</sup>) balance the negative charge of Al<sup>3+</sup> in IV-fold coordination [Xu and Van Deventer, 2003]. The dissolution of aluminosilicate materials from the surface of fly ash particles in a highly alkaline environment via hydrolysis is generally accepted as the first step in geopolymerisation [Duxon *et al.*, 2007], followed by oligomerisation, polymerisation, and finally, condensation of dissolved species. Geopolymers are a new class of materials that can be synthesised using metakaolin, natural minerals, and waste materials such as: fly ash, clay, slag, and red mud [Duxon *et al.*, 2007; Faheem *et al.*, 2013; Li *et al.*, 2010; He *et al.*, 2012]. Among these feedstocks, 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 to assess feasibility of geopolymer synthesis from fly ash from biomass by geopolymerisation method. The effect of temperature, curing time and the ratio of fly ash to alkaline activator (sodium hydroxide and sodium water glass) impact in the formability of geopolymers mass were investigated.

On the basic of the research investigations, optimal conditions of geopolymerisation have been determined.

## 2. Experimental

### 2.1. Material collection and preparation

The collection of samples of ash from the combustion of biomass (wood chips and waste of deciduous trees) was carried out in the CHP Arłamów (Poland). Primary ash samples (mass approx. 0.5 kg each) were collected from the base of the heaps ( $h = 0 - 50$  cm) from the bottom of holes with different depth (min. 50 cm). In order to get the average laboratory sample, the primary ash sample (10) were combined to give a general sample with mass approx. 5 kg. Then general sample were dried to get „air-dry” state in laboratory conditions (approx. 2 weeks). The laboratory sample with mass approx. 4 kg were prepared by “quartering” method.

### 2.2. Geopolymers preparation

Solid mixture composed of 50 weight parts of sand and 50 weight parts of biomass ash was prepared. Then, was dry blended until to get homogeneous mixture for approx. 10 minutes on a laboratory shaker Vibramax 100, (Heidolph, Niemcy). The alkaline solution was prepared by mixing sodium silicate with molar module  $\text{SiO}_2/\text{Na}_2\text{O}$  2.4 - 2.6 and density of 1.45 - 1.48  $\text{g}/\text{cm}^3$  (Chempur, Poland) with solid NaOH (reagent analytical grade, Chempur, Poland). It was stirred thoroughly and left to equalize concentrations and obtain a constant temperature (approx. 40 min). For the synthesis of geopolymers were used optimum molar module  $\text{SiO}_2/\text{Na}_2\text{O}$  aqueous solution of sodium silicate equal to 1.28, which was obtained by mixing sodium silicate with a solid NaOH in a ratio of 2:1. Then, to the alkaline solution was added solid mixture (ash with addition sand) and thoroughly mixed. Conditions for synthesis for each geopolymer sample were listed in Table 1. The ratio of alkaline solution to solid part (L:S,  $\text{cm}^3/\text{g}$ ) was as follows 10:90, 70:30, 50:50, 30:70 (descriptions of obtained geopolymers are presented in Table 1, respectively: PB10GEO, PB30GEO, PB50GEO, PB70GEO). The mixing time was approx. 30 minutes. When a homogenous, ductile consistency was obtained the mixture was inserted to cylindrical molds made from plastic material (PE) with dimensions 14x30 mm. The

samples were molded using manual pressure and in order to release air bubbles the samples were shaken for 15 minutes on a laboratory shaker. Tightly sealed molds were dried at different temperatures under atmospheric pressure or were heated in a laboratory drier (Table 1). After drying, the molds were removed. To avoid errors during the analyses 3 control samples were prepared in order to eliminate the possibility of an accidental phenomena affecting final results.

### 2.3. Materials characterization

SEM (Hitachi S-3400N) equipped with an energy-dispersive X-ray spectroscopy detector (EDS) was employed to determine the microstructure as well as chemical composition of the biomass ash and geopolymers.

UV-VIS-NIR absorption spectra of biomass ash and geopolymer, recorded in a reflectance mode, were obtained by using a Jasco V-670 spectrometer equipped with a diffuse reflectance attachment with an integrating sphere coated by  $\text{BaSO}_4$ .

## 3. Results and discussion

The obtained geopolymer from biomass ash is illustrated in Fig. 1. On the surface of some samples are visible white efflorescence caused by an excess of sodium oxide. Its occurrence is caused by the fact that the obtained sample geopolymers were in contact with the water contained in air, which migrates through the capillary forces, after some time evaporate from the surface and leave the sodium ions. They may react with the  $\text{CO}_2$  contained in the atmospheric air, and forming sodium carbonate [Kani *et al.* 2012]. It is possible to reduce or eliminate the occurrence of these "alkaline efflorescence" by replacing NaOH by another alkaline substance activating eg. KOH or by carried out on the final stage, additional heat treatment.

**Table 1.** The summary of raw materials and conditions of synthesis of geopolymers (description of symbols are in the text)

Type of geopolymer	Solid components ash/sand	Alkaline activator	Ratio L/S $\text{cm}^3/\text{g}$	Temperature of curing $^{\circ}\text{C}$	Time of curing h	Characetristic of blend
PB10GEO	1:1	Mixture of sodium silicate and solid	90:10	37	60	Very liquid consistency.
PB30GEO	1:1		70:30	40	51	Dense, plastic mass, difficult to form.
PB50GEO	1:1	NaOH	50:50	20	17	Liquid consistency, easy to form.
PB70GEO	1:1		30:70	60	43.5	Very liquid consistency.



**Figure 1.** Geopolymer obtained from biomass ash

### 3.1. Scanning electron microscopy

Ash, as a raw material to obtain geopolymers should not contain high levels of compounds such as sulfur compounds, unburned carbon, free calcium and iron compounds. If the iron is in the form of hematite or magnetite it may adversely affect to course of the pozzolanic reaction, because they are on the surface of the grains of fly ash and they hinder access of the liquid phase to the glassy phase [Garcia *et al.*, 2015]. In Figures 2 (a and b) and 3 (a and b) are presented the results of SEM analysis of the biomass ash and geopolymer obtained from the ash. Based on the analysis of SEM image of biomass ash (Fig. 2a), it was found that the diameter of the particles have different sizes, but not exceed 250  $\mu\text{m}$ . The ash is fine-grained, has an amorphous structure with aggregates. In Table 2 are presented the composition of the mineral phase of biomass ash and geopolymer on the basis of the ash. From Table 2 indicated that the biomass ash contains small amounts of aluminium oxide (0 - 10%) and silicon oxide (14 - 23%). It also contains trace amounts of MnO (less than 1%). It has a low content of iron and magnesium oxides (0 - 4%) and a relatively high content of potassium oxide (8 - 29%) and calcium (3- 25%).

The SEM image of geopolymer (Fig. 2b) showed that as a result of geopolymerization, structure becomes more porous and open in compare to biomass ash. In the structure are dominated aluminosilicates with size larger than 200  $\mu\text{m}$ . In comparison to biomass ash, in the obtained geopolymer are not occurred magnesium manganese and iron oxides. The content of potassium oxide (2.46%) and calcium oxide (3.63%) is much lower in comparison to ash from biomass. The silicon oxide is maintained at a similar level (16.88%). The lowest concentration found with aluminium oxide (1.09%).

### 3.2. Characteristics of obtained geopolymer

The properties of geopolymers depend on the kind of basic material used for their production, type and amount of activating solution and the conditions of geopolymerization reaction [Khale and Chaudhary, 2007]. The decisive role in the process of alkaline activation plays a molar ratio of  $\text{Al}_2\text{O}_3/\text{SiO}_2$ . The value of this molar ratio is substantially determined by the speed of the activation process and the type of products formed. From the research [Palomo *et al.*, 2003] follows that the very good results in

the synthesis of geopolymers are obtained with a low molar ratio of  $\text{Al}_2\text{O}_3/\text{SiO}_2$ . The molar ratios in obtained geopolymers from biomass ash are summarized in Table 3. From the presented data indicates that there is a clear difference in the molar ratios of  $\text{Al}_2\text{O}_3/\text{SiO}_2$ ,  $\text{SiO}_2/\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  for the geopolymers of the given ratio of alkaline solution to solid parts (L:S,  $\text{cm}^3/\text{g}$ ). On the basis of the molar ratio of  $\text{Al}_2\text{O}_3/\text{SiO}_2$ , it was found that the lowest value of the molar ratio shows geopolymer (PB70GEO), in which the volume of alkali solution to the mass of solid parts [ $\text{cm}^3/\text{g}$ ] is 30:70 (Table 1). The analysis of the literature data [Zivica *et al.*, 2014] shows that the optimum value of the molar ratio of  $\text{Al}_2\text{O}_3/\text{SiO}_2$  is 3.16 - 3.46, then obtained geopolymer exhibits better uniaxial compressive strength, which decreases with an increase in the ratio. When adopting this criterion for further studies were choose geopolymer (PB50GEO), in which the volume of alkali solution to the mass of solid parts [ $\text{cm}^3/\text{g}$ ] is 50:50 (Table 1).

The molar ratio  $\text{SiO}_2/\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  plays an important role in the mechanical properties of the resulting product. Mishra [2008] conducted experiments on FA based GPC by varying the concentration of NaOH and curing time. Total nine mixes were prepared with NaOH concentration as 8M, 12M, 16M and curing time as 24 hrs, 48 hrs, and 72 hrs. The investigation indicated: an increase in compressive strength with increase in NaOH concentration and curing time, increase in compressive strength after 48 hrs curing time not significant. Compressive strength up to 46 MPa was obtained with curing at 60°C. Water absorption decreased with increase in NaOH concentration and curing time. The molar ratio  $\text{SiO}_2/\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  plays an important role in the mechanical properties of the resulting product. By the increase of concentration of  $\text{Na}_2\text{O}$  or by reduction the concentration of silicate, is expected the increase strength, because the excess of sodium silicate makes difficult the evaporation of water and formation of structure of geopolymer. In the production of inorganic polymers content of  $\text{OH}^-$  ions in an alkaline solution contributes to the dissolution of ions  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  from fly ash, while  $\text{Na}^+$  ions contribute to the crystallization of zeolite type P [Zivica *et al.*, 2014]. Taking into account the values presented in Table 3, the lowest value of the molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  has geopolymer (PB10GEO), in which the volume of alkali solution to the mass of solid parts [ $\text{cm}^3/\text{g}$ ] is 90:10 (Table 1). All the obtained values of the molar ratio of  $\text{SiO}_2 / \text{Na}_2\text{O}$  are higher than the value

0.8, and so in reaction carried out at low temperature (20 °C) we obtained amorphous aluminosilicate or inorganic glass polymer [Zivica *et al.*, 2014], which was presented for geopolymer (PB50GEO), in which the volume of alkali solution the mass of solid parts [cm<sup>3</sup>/g] is 50:50 (Figure 1b).

The mechanism of geopolymerisation may be considered to occur in three stages [Xu and van Deventer, 2000]: dissolution, transportation or orientation, and polycondensation. The reactions of geopolymerisation take place through a series of exothermic processes [Palomo *et al.*, 1999] had observed that unlike conventional organic

polymers, glass, ceramic, or cement, the geopolymers are formed at low temperatures and they are non-combustible, heat-resistant, and fire/acid resistant. In performed studies it was found that to obtain the desired optimum consistency of geopolymers mass is possible for geopolymer (PB50GEO), in which the volume of alkali solution to the mass of solid parts [cm<sup>3</sup>/g] is 50:50. Taking into account conditions of synthesis presented in Table 1, the optimum temperature and time of the curing of this geopolymer is 20°C and 17 hours. The above mentioned was used in further analyses.

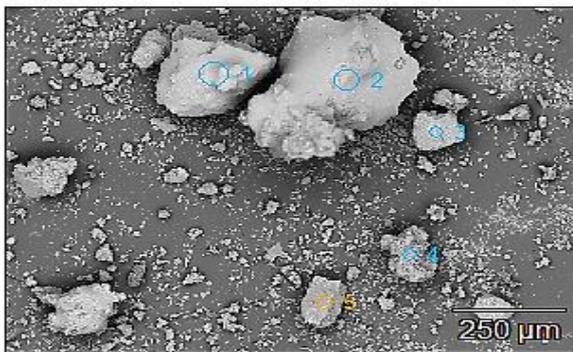
**Table 2.** The composition of the mineral phase of biomass ash and geopolymer getermined by EDS analysis

Study area	Content, %							
	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	MnO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O
<b>Biomass Ash</b>								
1	1.20	2.40	15.63	28.86	17.18	-	2.86	-
2	1.19	1.81	15.47	14.62	24.82	0.68	1.36	-
3	-	7.18	18.30	23.52	3.43	-	0.56	-
4	2.27	9.86	14.87	10.73	4.87	-	3.79	-
5	-	-	23.17	8.39	4.66	-	0.31	-
<b>Geopolymer from biomass ash (PB50GEO)</b>								
1		1.09	16.88	2.46	3.63			51.60

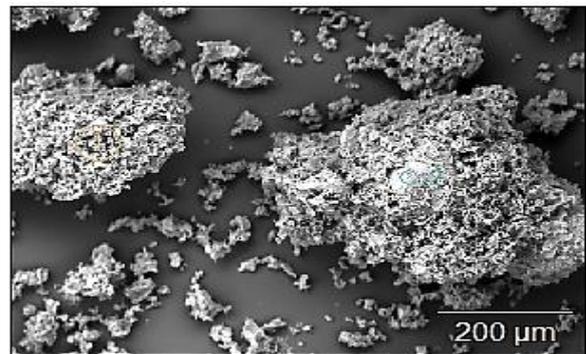
**Table 3.** The composition of geopolymers prepared from biomass ash

Type of geopolymer	Mole ratio		
	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	SiO <sub>2</sub> /Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> O
PB10GEO	7.55	1.25	1.10
PB30GEO	7.39	1.40	1.48
PB50GEO	3.50	1.53	1.75
PB70GEO	1.54	1.75	2.95

a)



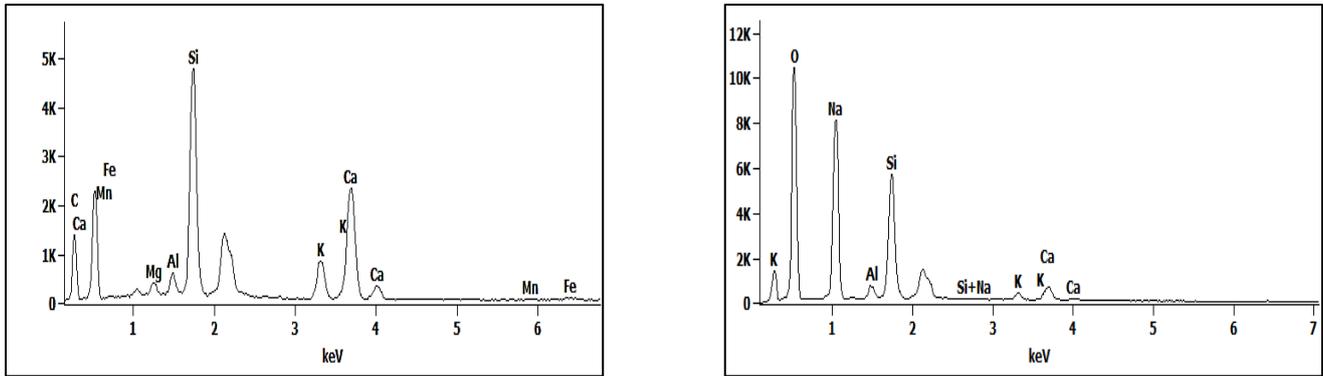
b)



**Figure 2.** SEM image of a) biomass ash, b) geopolymer from biomass ash

a)

b)



**Figure 3.** EDS spectra of a) biomass ash, b) geopolymer from biomass ash

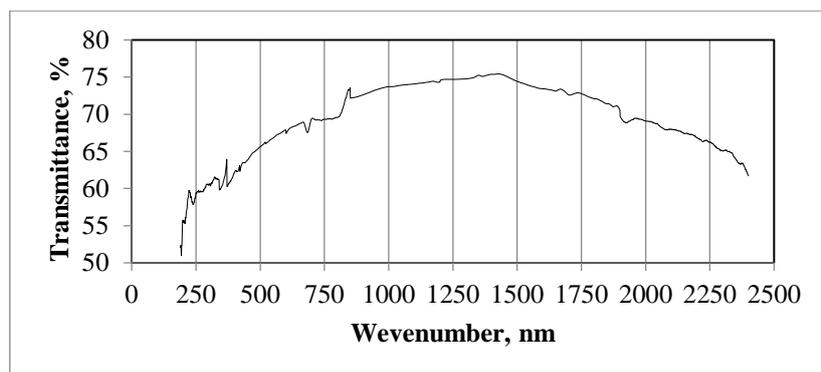
### 3.3. UV-VIS-NIR absorption spectra analysis

Figure 4 (a and b) shows the UV-VIS-NIR spectra of biomass ash and geopolymer. On the spectra vibrations originating from the skeleton of aluminum-silicon (~1500 nm, ~2000 nm) were found. The presence of a peak at a wavelength of approx. 1500 nm in the NIR area means that biomass ash and the resulting geopolymer are transparent to visible spectrum. This opens the possibility of using obtained geopolymers for optical and photocatalytic applications [Karamanis and Vardoulakis, 2012, Vardoulakis *et al.*, 2011]. From the presented spectra also results that transmittance of obtained geopolymers is higher compared to biomass ash (Figure 4a and b). The summary of the reflectance coefficients of light for different ranges of radiation, ie.  $SR_{UV}$  - in the UV range, ie. 280 - 400 nm;  $SR_{VIS}$  - in terms of VIS, ie. 400 - 700 nm;  $SR_{NIR}$  - in the NIR range, ie. 700 - 2500 nm are presented in Table 4. In the investigated materials reflectance

exceeded 60%. The value of reflectance for geopolymer - PBGEO (approx. 84%) is higher in all areas of the radiation in comparison to biomass ash - PB (approx. 74%). The largest difference was observed in the NIR, until 10%. From the obtained values of reflectance for obtained geopolymer from ash, follows that it has better optical and photocatalytic properties in comparison to ash from biomass.

The potential application of the obtained geopolymer from biomass ash as a cheap and efficient photocatalyst, active in the visible light range can be indicated. It also should be emphasized, that the processes of photocatalytic degradation of pollutants are a very promising method for the removal of environmental pollutants, due to the low cost, mild process conditions (temperature, pressure) and the ability to complete mineralization of contaminants [Hernández-Alonso *et al.* 2009; Yu *et al.* 2012].

a)



b)

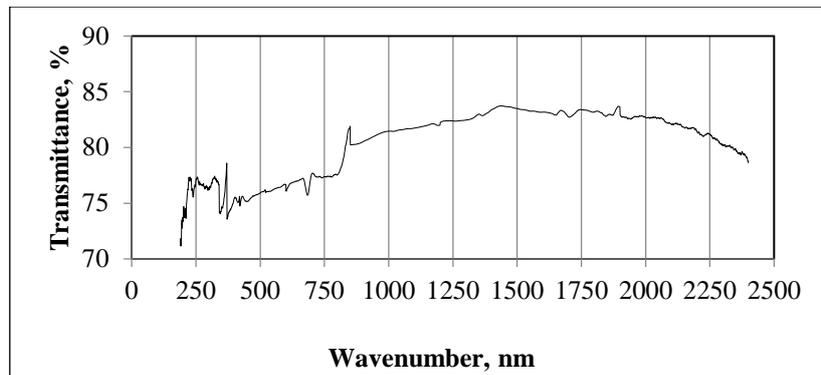


Figure 4. UV-VIS-NIR spectra of a) biomass ash b) geopolymer from biomass ash

Table 4. The summary of the reflection coefficients of light for investigated materials

Type of material	SR <sub>UV</sub> [%]	SR <sub>VIS</sub> [%]	SR <sub>NIR</sub> [%]
PB	65	68	74
PB GEO	75	76	84

#### 4. Conclusions

This paper investigated the assess feasibility of geopolymer synthesis from fly ash from biomass by geopolymerisation method. The effect of temperature, curing time and the ratio of fly ash to alkaline activator (sodium hydroxide and sodium water glass) impact in the formability of geopolymers mass were investigated. Assessed the studies performed, it was found that obtaining the desired dense plastic consistency of received geopolymers is possible under the following conditions, which are indicated as optimal: temperature - 20 °C, curing time 17 hours and the ratio of biomass ash [g] to alkaline activator [cm<sup>3</sup>] - 50:50.

To sum up:

- production of geopolymers based on ash from the combustion of biomass is a way of management of the waste from the energy industry, moreover, it reduces the influence of waste on the environment;
- geopolymers from biomass ash can be used as a cheap and effective photocatalysts active in the visible light.

Analysis of the available literature data on the potential use geopolymers, indicates that geopolymers obtained from biomass ash can be used in the process of heterogeneous photocatalysis, which is determined by adsorption of the reactants on the surface of the photocatalyst. Another research, which will be published in the future, will concern the assessment of the effectiveness of bonding (immobilization) of heavy metals using geopolymers obtained on the basis of the ash from the combustion of biomass.

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