Physicochemical Problems of Mineral Processing

Use of synthetic zeolite materials from fly ash to remove copper(II) ions from aqueous solutions

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Abstract: Water quality and waste management are two chief problems that the modern world is struggling with. Intensified development of the industry not only leads to the production of large amounts of solid waste that must be stored in landfills but can also result in contaminant emissions into the environment. Enormous quantities of ash produced from coal combustion have been a long-term problem of the industry. Literature studies show that fly ash can be used as a material to produce cheap and efficient zeolite-type adsorbents due to abundance of alumina-silicates in their composition. Fly ashes which were processed into zeolites as a result of alkaline hydrothermal treatment were obtained from two power plants in Poland (in *Turów* and *Zgierz*). The obtained zeolite materials and raw fly ash samples were characterised in terms of specific surface area, particle size distribution and density. The structure was also investigated using Fourier transform infrared spectroscopy (FTIR) in the mid-infrared wavenumber range. Two raw fly ashes and two zeolite materials were examined for their ability to remove Cu(II) ions from aqueous solutions. The results showed that the amount of adsorbed copper ions by alkaline-modified fly ash was higher than for unmodified fly ash. The ion removal efficiency is high and exceeds 95%.

Keywords: fly ash, copper(II), modification of fly ash, zeolite materials, adsorption

1. Introduction

Primary sources of environmental pollution by heavy metal ions are energy industry, agriculture, mining and processing of metal ores (Jaishankar, 2014). The contamination of groundwater with toxic metal ions is not desirable because of its negative impact on the living organisms (Markert et al., 2000). Therefore, the emission of metal ions should be minimalised by removing them from industrial wastewater to the lowest possible levels. One of the toxic heavy metals is copper (Mosby, 1996). Copper ions are considered toxic despite their crucial biological functions (Rensing, 2012) and usually found in the environment in small concentrations fulfilling biocenosis demand for this micronutrient. The source of contamination by copper ions is mostly mining and processing of metal ores. It is vital to remove trace copper ions from industrial effluents to preserve the environment and thereby human health.

Many methods of metal ions removal from aqueous solutions have been developed, including membrane processes, precipitation and filtration techniques, ion exchange processes and adsorption processes. One of the most efficient metal ion removal methods is adsorption (Bolisetty et al., 2019). Adsorption is a process that uses natural or synthetic materials with a large surface area to remove the desired substances through interaction between the removed molecule and the sorbent surface (Zhu et al., 2019).

Adsorbents for removal of heavy metal ions can be divided into several categories: natural minerals, synthetic minerals, carbon-based and biosorbents (Al-Qodah et al., 2017; Salam, 2019; Bolisetty et al., 2019). An example of natural mineral sorbents is natural zeolites. Zeolites are a group of crystalline minerals composed of hydrated aluminosilicates. Their crystalline structure is characterised by pores of

uniform dimensions (Peydayesh, 2013). The first synthetic zeolites were obtained as early as in the 19th century from volcanic ashes (Höller, 1970). However, it was not until 1987 that a paper was published describing the preparation of the synthetic zeolite from fly ash from coal incineration (Henmi, 1987). Already at that time, the waste from coal combustion was a severe problem (Tamanuki, 1980). In recent years, accordingly to sustainable management principles, many branches of science have been searching for applications for waste materials. The possibility of using fly ashes has recently met with increased interest among researchers. Fly ash, which due to its mineral composition could easily be transformed into synthetic zeolites, can be successfully used in heavy metal sorption (Sprynskyy et al., 2006; Koshy, 2016; Bai, 2019; Kobayashi, 2020; Chen, 2020). It fulfils the objectives of sustainable waste management because problematic waste becomes a product that can be used in wastewater treatment.

The scope of this paper is to establish whether it is possible to utilise zeolite materials produced from fly ash for Cu(II) removal from aqueous solutions. In this paper, a comparative study was performed of coal fly ash derived zeolites. The fly ash was sampled from the coal-powered power station in Turów *and Zgierz* (Poland). The materials were characterised by FTIR spectroscopy, microscopic photographs, particle size distribution and BET specific surface area. The adsorption properties of the obtained materials, such as adsorption capacity and Cu(II) removal efficiency, were investigated.

2.   Materials and methods

2.1. Materials

Fly ashes (FA) used for these studies were received from two power plants located in Poland and applying energy generation technology based on conventional coal combustion:
   a) **FA1** from *Turów* - burning brown coal in the pulverised coal furnace with calcium sorbents based desulphurisation system;
   b) **FA2** from *Zgierz* - burning brown coal and biomass in the fluidised bed furnace.

2.2. Methods and procedures

2.2.1. Alkaline hydrothermal modification

Hydrothermal zeolite synthesis requires the supply of Al and Si components as well as pure or mixed alkaline solutions. Important parameters of the zeolite production process, which also influence the type of crystallised phase are temperature, time, pressure and NaOH concentration.

The detailed procedure for obtaining zeolite material in this work was as follows: 25 g of fly ash (**FA1** or **FA2**) was joined with 500 cm^3 3.0 M aqueous solution of NaOH. The alkaline modification of fly ash was performed at 348 K over 24 hours. For both ash samples, after modification, the liquid phase was separated from the synthesis product and thoroughly washed using deionised water by filtration until a filtrate pH of 8 was obtained. Then was dried for one week at ambient temperature (298 K). Zeolite 1 (**Z1**) was obtained from the fly ash from the *Turów* fly ash and zeolite 2 (**Z2**) from the *Zgierz* fly ash.

2.2.2. Characterisation of fly ash and zeolite material

The specific surface area of fly ashes and zeolites was measured by the Brunauer-Emmett-Teller (BET) method for the helium/nitrogen mixture by using a FlowSorb II apparatus (Micromeritics). The particle size distribution of the investigated materials was determined using an LS 13 320 XR Particle Size Analyzer (Beckman Coulter). The chemical structures of both fly ash and zeolite materials before and after adsorption of Cu(II), were monitored by infrared spectroscopy applying Fourier Transformation (FT-IR) on a VERTEX 70v spectrometer (Bruker). The materials were investigated 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1}. The density of materials was determined using a pycnometer. The images of fly ash and zeolite material samples were done using an optical microscope Carl Zeiss Axio Imager M1.

2.2.3. Adsorption of Cu(II)

Research on adsorption was carried out applying a batch method for the following adsorbent weights: 0.05; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.75; 1.0, and 1.5 g. The fly ash or zeolite material sample was introduced into separate plastic bottles. Then, 10 cm^3 of the solution of Cu(II) (1000 mg/dm^3) at its native pH was

added to each sample. Next, the adsorbent was contacted with the solution for 24 h at 25°C. After this time, the suspensions were centrifuged, and the concentration of residual Cu(II) in the solutions was analysed.

All chemicals used in the present work were of analytical purity. The stock solution of Cu(II) was prepared in 1000 mg/dm³ concentration using $CuSO_4 \cdot 5H_2O$. The Cu(II) concentration in solution was analysed by using a laboratory ion-meter (CPI-505 ELMERON), equipped with an ion-selective electrode with a solid-copper membrane (Ecu-01 HYDROMET) and with a reference electrode (EAgCIP-311T EUROSENSOR). The experimental setup for the analysing of Cu(II) is shown in Fig. 1.
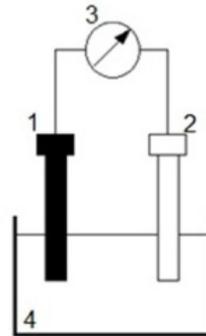
Fig. 1. The laboratory setup for analysing of Cu(II) concentration (1- the ion-selective electrode with a solid-copper membrane; 2- the reference electrode; 3- the laboratory ion meter; 4-the Cu(II) aqueous solution)

The adsorption Cu(II) capacity of adsorbents was calculated using equation (1):

$$q = \frac{(c_0 - c) \cdot V}{m} \tag{1}$$

where c_0 is the initial Cu(II) concentration of the solution (mg/dm³), c is the solution Cu(II) concentration after adsorption (mg/dm³), V is the volume of the solution (dm³), m is the dry weight of the adsorbent (g), and q is the adsorption capacity (mg/g).

The removal percentage was calculated based on the equation (2):

$$R = \frac{(c_0 - c)}{c_0} \cdot 100\% \tag{2}$$

where c_0 is the initial Cu(II) concentration of the solution (mg/dm³) and c is the solution Cu(II) concentration after adsorption (mg/dm³).

Comparative studies were conducted to determine adsorption of Cu(II) on the fly ashes and the zeolites.

3. Results and discussion

3.1. Characteristics of fly ash

In general, the fly ash samples have a common feature of fine particles and grey colour. Fly ashes used in the research is classified as silica-alumina ashes. According to ASTM, both FA1 and FA2 are classified as class C. This class includes fly ash resulting from the combustion of brown coal and usually containing significant amounts of CaO. Apart from pozzolanic properties, these ashes also exhibit hydraulic properties (Bhatt et al., 2019). The chemical compounds of fly ash were presented and discussed in previous works – for *Turów* (Polowczyk et al., 2010) and *Zgierz* (Polowczyk et al., 2017). The X-ray diffraction analysis of FA1 showed the presence of the following minerals: anhydrite, calcite, quartz and mullite. In turn, the X-ray FA2 analysis showed the presence of anhydrite, quartz, calcite and unburned carbon. The percentages of individual compounds are shown in Table 1. According to the XRD analysis, both ashes contain a significant amount of calcium compounds. It is related to the method of burning coal and desulphurisation in power plants. Fly ashes FA1 and FA2 are a specific type of ash. FA1 is ashes from flue gas desulphurisation processes where calcium sorbents are used, and fluidised combustion is combined with the desulphurisation process. Therefore, FA1 is enriched with large amounts of anhydrite and calcium oxide (Ostrowski, 2011). FA2 is produced through the co-

combustion of lignite and biomass in the fluidised bed furnace. Due to combustion, method FA2 is characterised by low Al_2O_3 content and significant amounts of anhydrite.

Observations under an optical microscope show large spheres of a glassy phase in the ash. However, this assessment is not entirely reliable, because very often, only the outer layers of ash grains are glassy. Fly ash is a material in which the proportion of amorphous phases is estimated at 60-80% (Singer and Berkgaut, 1995). The observation confirmed that significant amounts of quartz and anhydrite are present in the ashes. The images of investigated fly ash taken using the optical microscope are shown in Fig. 2. In Fig. 2, the diverse morphology of the ashes can be seen. There are both spherical forms with a diameter of about 20 μm and numerous grains of irregular shape. Their size is from 2 to 40 μm. The spherical forms are mainly aluminosilicates, and the surfaces of these particles are mostly smooth, rarely rough. The fly ash from *Zgierz* contained less amount of spherical forms than fly ash from *Turów*. It dominantly contains irregular, porous sponge-like particles of unburned carbon. In Fig 2B crystalline, star-shaped particles are visible.
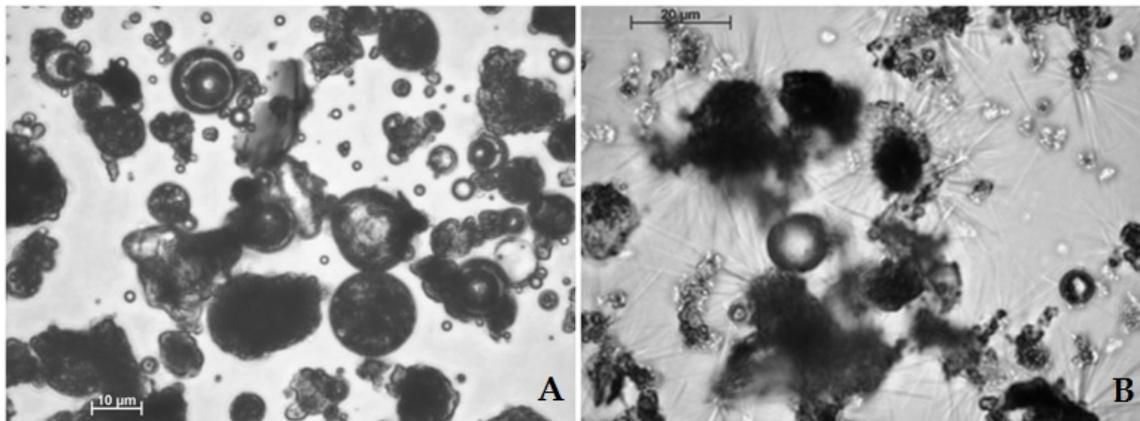
Fig. 2. The images of fly ash A) **FA1**, B) **FA2** (under magnification x100)

Particle size analysis of FA1 showed a median diameter (d_{50}) of about 37 μm, while d_{10} and d_{90} were 4.0 and 120 μm, respectively. FA2 particle size analysis showed a median diameter (d_{50}) of about 106 μm, while d_{10} and d_{90} were 18 and 213 μm, respectively. Additionally, a parameter, which shows the width of the size distribution (the span), was calculated. The span of volume-based size distribution is defined as:

$$span = \frac{d_{90} - d_{10}}{d_{50}} \tag{3}$$

The span gives an indication of how far the 10% and 90% points are apart, normalised with the midpoint. Merkus offers six ranges of the width of the size distribution in his classification (Merkus, 2009):

- dimensional   < 1.02
- very narrow   1.02 – 1.05
- narrow   1.05 – 1.5
- average   1.5 – 4.0
- wide   4.0 – 10
- very wide   > 10.

The determined span values for FA1 and FA2 indicate the mean width of the particle size distribution are 3.16 and 1.84, respectively. The d_{10}, d_{50} and d_{90} values and the calculated size distribution span are presented in Table 1. The width of the particle size distribution for both tested ashes is in the average range. The density of FA1 and FA2 was determined using a pycnometer, and it amounts to 2.70 and 2.62 g/cm^3, respectively. The specific BET surface area was 2.35 and 17.82 m^2/g for FA1 and FA2, respectively.

The presented characteristics of fly ash clearly show that the materials used in the research are specific. They are characterized by a high content of anhydrite and calcium oxide, which may negatively

affect the formation of zeolite materials. Besides, they are distinguished by a small specific surface. Therefore, the conducted research was aimed at checking whether it is possible to produce zeolites from such fly ash, which will be a suitable adsorbent for heavy metal ions.

Table 1. Chemical and physical properties of fly ashes

Parameters	*Turów*	*Zgierz*
	FA1	**FA2**
Density [g/cm³]	2.70	2.62
Specific BET surface area [m²/g]	2.35	17.82
Particle size distribution	d_{10} = 4.0 μm d_{50} = 36.7 μm d_{90} = 120 μm	d_{10} = 17.8 μm d_{50} = 105.5 μm d_{90} = 212.6 μm
Width of the size distribution	span = 3.16	span = 1.84
Chemical composition	anhydrite 46.8% calcite 2.6 % quartz 31.2 % hematite 1.6 % calcium oxide 17.8 %	anhydrite 44.2 % calcite 2.4 % quartz 29.5 % hematite 1.5 % calcium oxide 16.9 % unburned carbon 5.5%
Particle shape	spherical irregular	spherical irregular crystalline, star-shaped

3.2. Characteristics of zeolite materials

After modification of fly ashes with NaOH solution, new materials were obtained. The analysis of particle size distribution showed that after the synthesis, the formed materials are finer than the raw fly ash. The calculated size distribution *span* suggests that the obtained zeolites are characterised by narrower particle size distribution than raw fly ash. According to the Mercus classification, it is still an average width. The specification of four characteristic parameters of particle size distribution, including d10, d50, d90 and span, are given in Table 3. The density of obtained zeolites was also determined and was found to be 2.00 g/cm³ and 2.15 g/cm³ – for Z1 and Z2, respectively. The density of ash FA1 is also lower than the density of FA2. The specific surface area of the produced zeolites was also determined to check the influence of the modification on this parameter. As can be seen from the obtained results, the specific surface area of the synthesised zeolites is much larger than that of the raw fly ash, and it is 24.78 m²/g and 65.10 m²/g, for Z1 and Z2, respectively. It is worth to note that the specific surface area for Z1 is ten times higher and for Z2 three times higher compared to the initial material. According to Franus, an increase in the surface area during the synthesis of zeolite results from the micropore's texture with the zeolite structure (Franus, 2012). The specific surface area of zeolites obtained from fly ashes is relatively low compared to the literature data. The specification of fly ash has a significant influence on the range of the specific surface area of zeolites obtained by alkaline-hydrothermal modification. In the literature, there can be found information about zeolites which are characterized by low specific surface area, below 45 m²/g (Kobayashi et al., 2020; Koshy and Singh, 2016) and very large, above 250 m²/g (Kyzioł-Komosińska et al., 2015; Ojha et al. al., al., 2004). Commercial zeolite 13X is characterized by a specific surface area of about 478 m²/g.

The pictures were taken to show changes in material morphology. Both Z1 and Z2 have more glassy phase than raw ashes. The absence of the spherical particles in tested fly ash indicates the high conversion of fly ash to crystalline zeolite through hydrothermal treatment. As can be seen from Fig. 3, the crystal phase of the obtained zeolite can be determined as irregular. In the literature it can be found that the morphological forms of Na-X zeolite are often needle-like crystals about a few micrometres in size, creating a pattern resembling that like a skein of wool (Franus, 2012), which are visible to the obtained zeolite material. The images of zeolites taken using the optical microscope are shown in Fig. 3.

Table. 2. Physical properties of obtained zeolite materials

Parameters	*Turów*	*Zgierz*
	Z1	**Z2**
Density [g/cm³]	2.00	2.15
Specific BET surface area [m²/g]	24.78	65.10
Particle size distribution	$d_{10} = 4.2$ µm $d_{50} = 17.0$ µm $d_{90} = 44.6$ µm	$d_{10} = 13.9$ µm $d_{50} = 34.7$ µm $d_{90} = 72.0$ µm
Width of size distribution	span = 2.38	span = 1.67
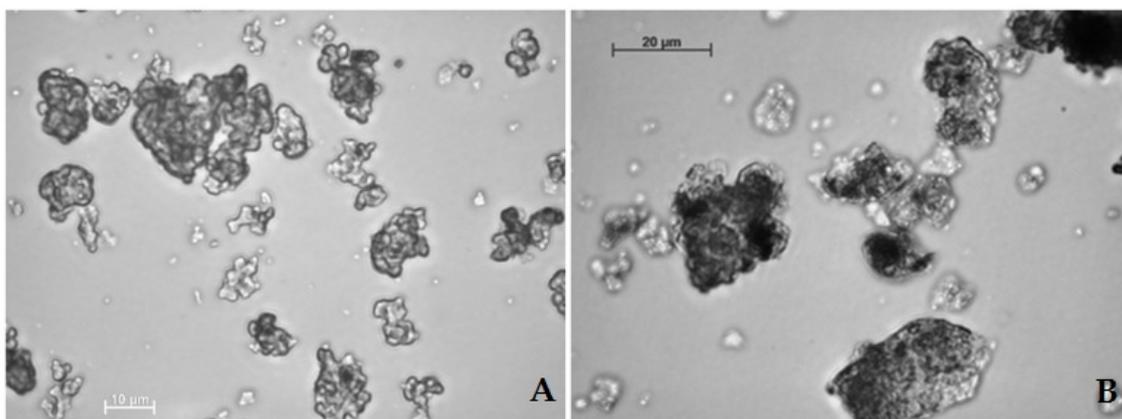
Fig. 3. The images of obtained zeolites A) **Z1** B) **Z2** (under magnification x100)

3.3. Adsorption of Cu(II)

The sorption capacity of untreated fly ash and these modified with NaOH solution against Cu(II) ions was checked. The obtained results are presented in Table 3. All the experiments with adsorption of Cu(II) were carried out at pH around 5.5 since actual wastewater containing copper ions usually has an acidic pH.

Studies on the sorption capacity have proved that it is possible to remove Cu(II) from aqueous solutions with FA1 and FA2. FA2 proved to be better adsorbent than FA1, in this respect. For FA1, the maximum removal was achieved with the highest dose of adsorbent (1.5 g) and was at 63%. In contrast, FA2 reaches over 90% removal of Cu(II) from the solution at 0.1 g of adsorbent. With 1.5 g, the removal rate is almost 100%. For both FA1 and FA1, the highest value of sorption capacity was obtained with the lowest dose of the adsorbent. For FA1 it was 6.63 mg/g and for FA2 17.88 mg/g, respectively. The significant difference in the achieved sorption capacity is related to the difference in specific surface area of FA2, which is three times greater than FA1 (Table 3). For both adsorbents (FA1 and FA2), it can be noted that the adsorption capacity was found to decrease proportionally with an increase in the quantity of fly ash. However, the Cu(II) removal effectiveness of fly ashes increases with the adsorbent amount. This may be due to many vacant active sites on adsorbents surface. As the initial concentration of Cu(II) is constant, Cu(II) ions can only occupy a certain number of active sites.

Subsequently, Cu(II) sorption tests were carried out using the produced zeolites. It was observed that with Z1, the removal of Cu(II) from aqueous solutions was more effective than with unmodified fly ash (FA1). At the highest dose of adsorbent (1.5 g) more than 98% removal efficiency was achieved, while previously only 63.20%. Higher sorption capacity of 9.50 mg/g was also approached. Z2, on the other hand, achieves similar efficacy as unmodified fly ash (FA2).

Comparing the sorption capacity of fly ashes and zeolite materials can be concluded that modification with NaOH solution is beneficial only for fly ash from *Turów*. In the case of fly ash from *Zgierz*, its processing into zeolite is not profitable. The high Cu(II) removal efficiency of raw fly ash suggests that it can be used without unnecessary costs associated with zeolite synthesis. It is, therefore, necessary to verify whether both fly ash and zeolite will be equally useful as adsorbents for other pollutants, especially heavy metal ions.

Table 3. Results from Cu(II) adsorption experiment (initial Cu(II) concentration: 1000 mg/dm³; adsorbent dose: 0.05 – 1.5 g; pH 5.5; T=25±1°C)

weight of adsorbent	Turów				Zgierz			
	FA1		Z1		FA2		Z2	
[g]	[mg/g]	[%]	[mg/g]	[%]	[mg/g]	[%]	[mg/g]	[%]
0.05	6.63	33.16	9.50	47.50	17.88	89.38	18.48	92.41
0.1	4.15	41.50	5.25	52.50	9.32	93.17	9.32	93.17
0.2	2.47	49.47	3.46	69.20	4.77	95.45	4.70	93.93
0.3	1.80	54.02	2.63	78.83	3.21	96.21	3.16	94.69
0.4	1.47	58.80	2.19	87.48	2.42	96.97	2.39	95.45
0.5	1.19	59.26	1.87	93.40	1.95	97.72	1.92	96.21
0.6	1.01	60.85	1.61	96.74	1.64	98.10	1.62	96.97
0.75	0.82	61.84	1.30	97.65	1.31	98.48	1.30	97.72
1.0	0.62	62.29	0.98	98.41	0.99	99.24	0.98	98.48
1.5	0.42	63.20	0.66	98.94	0.66	99.24	0.66	99.24

It was also investigated how the specific surface area of the adsorbents used changes after Cu(II) sorption. Both for fly ash (FA1 and FA2) and zeolites (Z1 and Z2) an increase in the specific surface area was observed after sorption tests. This is probably due to the swelling of the adsorbent during sorption by adding an acidic solution of Cu(II). A similar phenomenon was observed by Lassesson and co-workers (Lassesson et al., 2014).

3.3. Mechanism of Cu(II) adsorption on fly ash and zeolites

To rightly understand how the converting of fly ash influences its usability for the removal of Cu(II), it is necessary to describe the issue of the adsorption mechanism. Besides the process parameters, such as pH, temperature, initial Cu(II) concentration in the solution, an adsorbent characteristic plays a crucial role in the adsorption mechanism.

As reported by Pan and co-workers, the hydrous aluminium oxide and silicon oxide in the surface of fly ash can complex with metal ions by chemical bonding. Their reactions to Cu(II) can be presented as follows (Pan et al., 2003):

$$\equiv SiO + Cu^{2+} \leftrightarrow \equiv Si\text{-}O\,Cu^{2+} + H^+ \tag{4}$$

$$\equiv Si\text{-}O + Cu^{2+} \leftrightarrow Si\text{-}O\,Cu^{2+} \tag{5}$$

$$2(\equiv Si\text{-}OH) + Cu^{2+} \leftrightarrow (\equiv Si\text{-}O)_2\,Cu^{2+} \tag{6}$$

$$2(\equiv Si\text{-}O) + Cu^{2+} \leftrightarrow (\equiv Si\text{-}O)_2\,Cu^{2+} \tag{7}$$
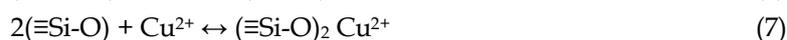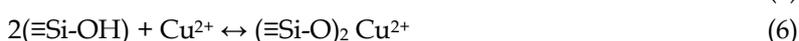
In turn, a possible cation-exchange mechanism can be expected in the zeolite structure, where there are more Na^+ sites available for cation exchange, as shown below (Sahoo et al., 2013):

$$Z - Na + M^+ \rightarrow Z - M + Na^+ \tag{8}$$
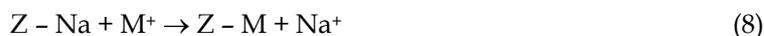
where M is the metal cations (in this case, Cu^{2+}).

3.4.1. Discussion of the FTIR spectra

The characteristic FT-IR vibration bands and their interpretation for fly ash and zeolite were presented in Table 4 (Malonda Shabani et al., 2019; Alehyen et al., 2017; Polowczyk et al., 2017; Hałas et al., 2017; Król et al., 2016; Naikoo, 2016; Chindaprasirt et al., 2009; Ojha et al., 2004; Barnett et al., 2002; Henmi, 1987).

Detailed description of individual bands of fly ashes and zeolite materials before and after Cu(II) adsorption are discussed below. FT-IR spectra of raw fly ashes (FA1 and FA2) and synthesized zeolites (Z1 and Z2) before and after Cu(II) adsorption are presented in Fig. 4.

In the case of FTIR spectra measured for fly ash from Turów coal-powered power station (FA1), there are distinctive peaks at 1060 cm⁻¹, 750 cm⁻¹, 550 cm⁻¹ and 450 cm⁻¹. The bands at 1095 cm⁻¹ can be attributed to the quartz phase presence (Malonda Shabani et al., 2019). Si- or Al-O bending vibrations

Table 4. Position of main peaks in FTIR spectra of fly ash and zeolite

Fly ash		Zeolite	
Adsorption bands	Interpretation	Adsorption bands	Interpretation
3700 – 3400 cm^{-1} 1600 cm^{-1}	-OH and H-O-H groups and adsorbed water molecules on the surface of fly ash	3700 – 3400 cm^{-1}	zeolite or hydration water
1120 cm^{-1}	S-O bonds	1480 – 1400 cm^{-1} 875 cm^{-1}	C-O bonds
1095 cm^{-1}	quartz phase	1300 – 900 cm^{-1}	aluminosilicate chase
680-590 cm^{-1}	Si-O-Si bonds	750 and 670 cm^{-1}	zeolite type X phase
500-450 cm^{-1}	Si-O or Al-O bonds	570 cm^{-1}	zeolite type A phase
460 cm^{-1}	O-Si-O bonds		
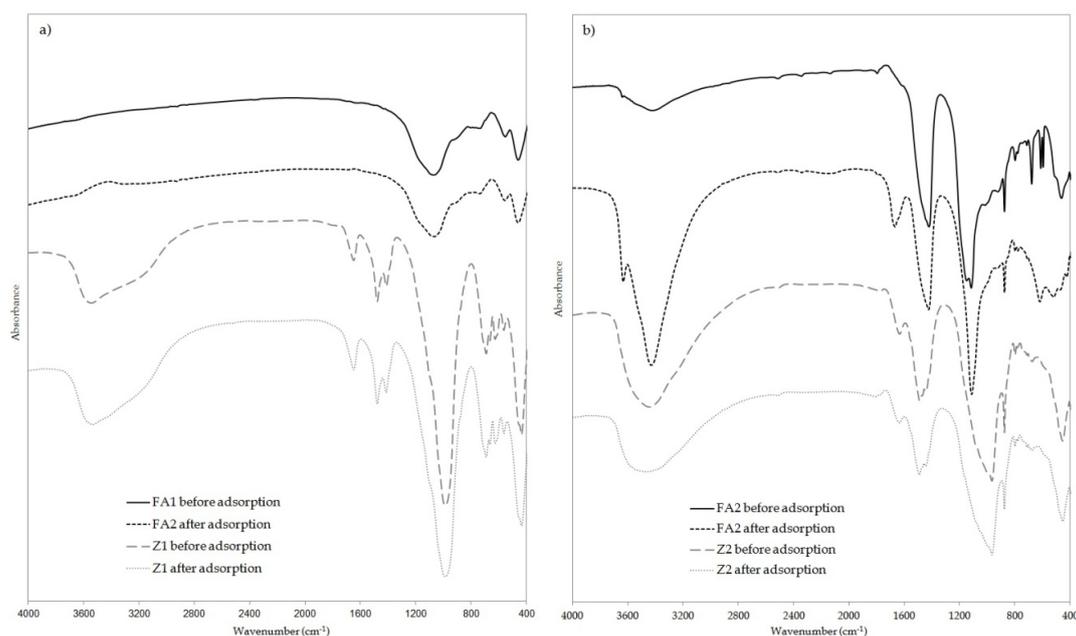
Fig. 4. FTIR spectra of adsorbents before and after Cu(II) adsorption: a) *Turów*, b) *Zgierz*

were detected between 450-500 cm^{-1} (Malonda Shabani et al., 2019; Alehyen et al., 2017; Ojha et al., 2004). There are no significant differences between FTIR spectra for raw fly ash and fly ash after Cu(II) adsorption. That indicates that the structure remained unchanged through the process and is stable.

In fly ash from *Zgierz* coal-powered power station (FA2) which underwent changes during the adsorption process, the most evident differences in FTIR spectra are seen in a range of 3400-3700 cm^{-1} and 1110-1200 cm^{-1}. In material after Cu(II) adsorption band 1640 cm^{-1} can be observed, this band is attributed to H-O-H bending vibration. The stretching vibration with 3400 cm^{-1} O-H can be explained by the appearance of hydroxy-sodalite phase that builds a zeolite structure (Hałas et al., 2017; Henmi, 1987). In FTIR spectra of FA2, there can be seen transmittance drop at frequency 1120 cm^{-1}, this is not visible in the spectra of FA2 after adsorption. This adsorption band is usually attributed to S-O bonds in minerals like ettringite (Barnett et al., 2002). The lack of 1120 cm^{-1} absorption band in material sampled after adsorption could be attributed to chemical structure change that fly ash underwent during the adsorption process. Another significant change can be seen in range 680-590 cm^{-1} it could be attributed to changes in Si-O-Si bridges (Polowczyk et al., 2017). Other difference can be noticed in the band 460 cm^{-1}, where O-Si-O bending vibrations can be usually observed (Chindaprasirt et al., 2009). Significant changes between FA2 and FA2 after the Cu(II) adsorption could implicate that fly ash is not stable chemically during the sorption process and undergoes a structural transformation.

FTIR spectra of Z1 and Z2 show that all four samples have pronounced absorption bands in range 3500-3400 cm^{-1} which is attributed to O-H bond of zeolite water or hydration water. In all zeolite samples,

there is evidence of C-O bonds from carbonate groups at bands seen as doublets in the range 1480-1400 cm^{-1}. Another evidence of C-O bonds from carbonate groups is visible at 875 cm^{-1} thought it is more explicit in Z2 spectra (Barnett et al., 2002). Absorption bands in range 1300-900 cm^{-1} indicate the presence of aluminosilicates (Naikoo, 2016). Further analysis of Z2 spectra can indicate that zeolite-X has formed as there are bands present at 750 cm^{-1} and 670 cm^{-1}, those bands are attributed to zeolite-X structures (Król et al., 2016). In the case of Z1 FTIR spectra, bands indicating the presence of zeolite-X are not visible. However, the band indicating the presence of zeolite is visible at 560 cm^{-1} (Król et al., 2014). In case of both materials FTIR spectra show vibration bands in a range of 500-400 cm^{-1}, those bands are attributed to Si-O-Si or Si-O-Al bonds present in aluminosilicate phase.

4. Conclusions

The hydrothermal method of zeolite synthesis from fly ash is efficient and straightforward. This method allows for utilising problematic waste from coal combustion to produce a valuable product that could be used in wastewater treatment. The obtained materials were characterized, and then adsorption tests were conducted at the native pH of Cu(II) ions solutions. The modified materials have better adsorption properties than raw fly ash. The main advantage of the modified materials is their chemical stability during adsorption. According to FTIR spectra of raw fly ash and synthesised zeolites, fly ashes are not stable during adsorption process as whole spectra before and after adsorption differ significantly. However, in the spectra obtained from the zeolite, the results show that the absorption bands remain unchanged after Cu(II) adsorption, which indicates greater stability of these products than raw materials. Obtained zeolites apart from chemical stability have also slightly better sorption capacity towards Cu(II) ions than raw fly ashes. The surface area of materials was significantly increased through the modification according to BET measurements. Compared to other zeolites described in the literature (Kyzioł-Komosińska et al., 2015), Z1 and Z2 zeolites have a rather low sorption capacity in native pH of the Cu(II) ions solutions. However, the scope of this research was exploring the possibility of repurposing fly ashes from *Turów* and *Zgierz* coal-powered power stations. Obtaining of zeolite materials was successful as it was confirmed on FTIR spectra that material obtained from FA1 (*Turów*) had zeolite A phase and material synthesized from FA2 (*Zgierz*) contained zeolite X phase. The adsorption process, with the use of obtained materials, needs to be optimized and investigated further. Possibility of zeolite synthesis from fly ashes is a promising alternative to exploiting natural deposits of zeolite minerals which is expensive and leads to devastation of the environment. Repurposing problematic coal combustion waste to a substrate for zeolite materials fulfils the objectives of sustainable waste management and ultimately could lower the impact of anthropogenic activity on the environment.

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