

Optimized Production of Coal Fly Ash Derived Synthetic Zeolites for Mercury Removal from Wastewater

Z Tauanov^{1,3}, D Shah¹, G Itskos² and V Inglezakis^{1,3}

¹School of Engineering, Chemical Engineering Department, Environmental Science and Technology Group (ESTg), Nazarbayev University, Astana, 010000, Kazakhstan

²School of Materials Engineering, Purdue University, West Lafayette, IN 47907-2045, USA.

³Corresponding authors: zhtauanov@nu.edu.kz; vasileios.inglezakis@nu.edu.kz

Abstract. Coal fly ash (CFA) derived synthetic zeolites have become popular with recent advances and its ever-expanding range of applications, particularly as an adsorbent for water and gas purification and as a binder or additive in the construction industry and agriculture. Among these applications, perpetual interest has been in utilization of CFA derived synthetic zeolites for removal of heavy metals from wastewater. We herein focus on utilization of locally available CFA for efficient adsorption of mercury from wastewater. To this end, experimental conditions were investigated so that to produce synthetic zeolites from Kazakhstani CFAs with conversion into zeolite up to 78%, which has remarkably high magnetite content. In particular, the effect of synthesis reaction temperature, reaction time, and loading of adsorbent were systematically investigated and optimized. All produced synthetic zeolites and the respective CFAs were characterized using XRD, XRF, PSA and porosimetric instruments to obtain microstructural and mineralogical data. Furthermore, the synthesized zeolites were studied for the removal of mercury from aqueous solutions. A comparison of removal efficiency and its relationship to the physical and chemical properties of the synthetic zeolites were analyzed and interpreted.

1. Introduction

Coal fly ash (CFA) is a by-product from combustion of coal in electric power stations all over the world. The amount of annually discharged CFA is enormous and thus it requires further investigation on the reprocessing of CFA as it causes serious environmental and health problems [1-3]. One efficient way of converting CFA into a value-added product is synthesizing zeolites [4-7], which have a wide range of application fields including agriculture, environment and industry [8]. A number of successful studies on pilot-scale or industrial production of synthetic zeolites from coal fly ash have been conducted already [9-11]. According to these studies it is practical and economically feasible to manufacture zeolitic adsorbents from coal fly ash that allows promising utilization solution for this by-product of coal combustion [11]. Thus, all these studies imply the necessity for production of synthetic zeolites in large quantities to effectively utilize value-added raw material.

Synthetic zeolites could be produced using various raw materials as clay minerals [12-14], siliceous minerals [15] and waste materials as coal fly ash [2, 4, 7, 8, 16]. Among the available raw materials coal fly ash is considered as one of the suitable due to low cost, abundance and possibility to produce various zeolites depending on reaction conditions [11], in contrast to natural zeolites that require costly modifications in order to be suitable for industrial application.

The chemical composition of zeolite and CFA is almost the same, but the major difference between these two is the structure: CFA is mainly composed of amorphous structure, while zeolite has a well-defined crystalline structure [17]. Moreover, zeolite has higher cation exchange capacity (CEC), larger surface area and demonstrates superior thermal stability [18] that further enhances the utilization



sectors. Over the past decades there have been numerous studies on the synthesis of zeolites from coal fly-ash and one of the widely used methods for production is the hydrothermal conversion using alkaline solutions [8, 19, 20]. There are several other emerging synthetic methods in laboratory scale production as microwave-assisted [2] and ultrasound-assisted production [4, 21, 22], fusion followed by hydrothermal synthesis [23-26] and salt-thermal production [27]. However, hydrothermal synthesis, which is multiphase crystallization process including both amorphous and crystalline solid phases and at least one liquid phase [28], is still the most promising and widely applied method, which is positioned in the core of all of the above mentioned production methods. According to this method the raw coal fly ash is dissolved in alkaline solution such as NaOH or KOH to extract aluminate and silicate constituents and then undergoes heat treatment to produce zeolite crystals [10, 17]. There are several parameters that substantially affect the zeolitization process as reaction temperature and time, Si/Al ratio in the raw fly ash and alkaline solution pH [8, 19, 20, 29]. Depending on these reaction conditions it is possible to obtain various synthetic zeolites, such as zeolite A [6], zeolite Na-P [4], sodalite [30] and many other types of synthetic zeolite.

Despite the fact that there are numerous studies that have already been published the underlying mechanism of zeolite formation and production process are still not well-studied. The questions as how the above-listed main parameters affect the mechanism of zeolite formation and in which way it should be controlled in order to obtain the highest possible conversion from fly ash to synthetic zeolite is not sufficiently explained in literature. Moreover, to the best of our knowledge, there has been no optimization studies conducted based on experimental results that will inherently assist in better understanding of zeolitization mechanism and in finding optimum reaction parameters, which correspondingly emphasizes the necessity for this type of research. In addition, the authors aim to study the removal one of the less investigated heavy metals, namely mercury (II) ions from aqueous solutions.

In this paper, we aim to optimize the zeolitization process based on experimental results from several different recent references and experimental work carried out in this study by following factorial analysis approach. All produced and raw materials were characterized by means of advanced microstructural and mineralogical characterization instruments. The most successful synthetic zeolites based on conversion yield from raw CFA and purity of the product were tested in batch reactors for the removal of mercury (II) ions from aqueous solutions.

2. Materials and methods

2.1. Materials

A representative coal fly ash (CFA) sample was collected from the electrostatic precipitators of coal-fired power plants of Astana (Ekibastuz CFA or E-CFA) and Oskemen (Karazhyra or K-CFA and Maikuben CFA or M-CFA). Both cities are under maximum electricity load. All CFA samples were used as received without preliminary washing and sieving. Prior to experiment CFA samples were homogenized and dried in oven at 70 °C for 12 h. The sodium hydroxide of analytical grade (Fischer Scientific, pearls, >97%) was used to prepare an alkaline solution with various concentrations.

2.2. Methods

2.2.1. Zeolite synthesis

The E-CFA of Astana city power plant was selected to study the effect of reaction parameters and to optimize production of synthetic zeolites (ZFAs), while after setting optimum parameters for production the other two CFAs were processed and used in the adsorption experiments. To produce synthetic zeolite (ZFA), E-CFA underwent a conventional alkaline hydrothermal treatment at 90-110 °C, using NaOH with concentrations of 1M or 3 M as an activation solution, in a 1L heavy-walled glass reactor. The incubation period was set at 24 or 48 hours and a mixing rate was set constant at 126 rpm for all experiments. After set period, the mixture was filtered and washed several times until no NaOH was detected. To study the factorial effect of 3 parameters, namely the reaction temperature, time and loading ($C \cdot V/m$, mole/g) on conversion rate of CFA into ZFAs 8 experiments were conducted in duplicate (table 1).

Table 1. Parameters applied to convert E-CFA into E-ZFA – Factorial analysis.

Experiment	Zeolite acronym	Temperature, °C	Time, h	Loading, mole/g
1	ZFA_1M_50g_90C_126rpm_24h	90	24	0.02
2	ZFA_1M_50g_110C_126rpm_24h	110	24	0.02
3	ZFA_1M_50g_90C_126rpm_48h	90	48	0.02
4	ZFA_3M_50g_90C_126rpm_24h	90	24	0.06
5	ZFA_1M_50g_110C_126rpm_48h	110	48	0.02
6	ZFA_3M_50g_110C_126rpm_24h	110	24	0.06
7	ZFA_3M_50g_90C_126rpm_48h	90	48	0.06
8	ZFA_3M_50g_110C_126rpm_48h	110	48	0.06

2.2.2. Mineralogical characterization

X-Ray Diffraction (XRD) instrument was used to obtain information on mineralogical phases present in CFA and ZFA. The samples analyzed include synthetic zeolites produced from E-CFA of Astana power plant, K-CFA and M-CFA of Oskemen power plant. The CFA samples were analyzed as received without prior purification and sieving, while synthetic zeolites were washed and dried before analysis. The XRD pattern was recorded on a SmartLab X-ray diffraction instrument (Cu, K- β filter, 40 kV and 30 mA) with a diffraction angle of 2θ and a scanning range of 5–100° (Rigaku, Japan). Phase identification was made by utilizing the Auto-search option of powder diffraction file library.

X-Ray Fluorescence (XRF, PANalytical Axios) instrument was applied to get the elemental composition of CFAs and ZFAs. The CFA sample was analyzed as received without prior purification and sieving whereas all produced ZFAs were washed and dried beforehand. The ratio of sample with binder was set at 10 g to 3 g (total mass of 13 g) with a diameter of pellet at 5 cm and thickness of pellet at 0.5 cm. The analyses were duplicated and conducted under inert atmosphere.

2.2.3. Microstructural characterization

Particle size analysis (PSA, Malvern Mastersizer 3000) instrument was used to obtain the information on volumetric percentage of each particle size and their distribution across the range of 0.01 μm to 10 000 μm . Distilled water was used as a dispersant for all samples in Hydro-MV mode.

A Nitrogen Porosimeter Autosorb-1 was applied to obtain data on specific surface area (SSA), average pore size and total specific volume. Three widely applied approaches of calculation namely BET, BJH and DFT were used for analysis of raw data. The samples were first degassed for 2-3 hours prior to analysis at stepwise heating from 50 °C to 200 °C. A 9 mm glass cell without rod was used for all porosimetric studies.

2.2.4. Batch adsorption studies

Mercury (II) solution with 10 ppm concentration was used throughout the study unless otherwise reported. Mercury analyzer (Lumex RA-915M) was used to quantify the amount of mercury adsorbed. All adsorption experiments were carried out in duplication without any stirring and at room temperature. The initial volume of mercury (II) solution was 40 mL and adsorbent amount 0.3 g. After a certain period of time, 0.15-0.2 mL of samples were sampled from the batch reactors for analysis. In all of adsorption experiments, to examine the possible effect of container walls on adsorption a glass and plastic (polypropylene) containers were used. A reference control solution with the same initial concentration of 10 ppm and reference-deionized water with the same pH and adsorbents were used to compare and eliminate any deviation. The total volume of solutions withdrawn was kept to a minimum (1.8 mL) in order to not disturb the initial m/V ratio.

3. Results and discussion

3.1. Zeolite synthesis

Table 2 summarizes the zeolite synthesis results obtained under different reaction conditions. In general, it is noticeable that the effect of reaction temperature and loading is significant with parameter sets No. 6 and 8 demonstrating the highest yield.

Table 2. Zeolite synthesis optimization: Factorial analysis

Experiment No.	Temperature, °C	Time, h	Loading, mole/g	Zeolite yield (% , average of duplication)	Factors effect, %
1	90	24	0.02	19.80	0
2	110	24	0.02	45.30	25.50
3	90	48	0.02	48.25	28.45
4	90	24	0.06	39.60	19.80
5	110	48	0.02	47.00	27.20
6	110	24	0.06	55.90	36.10
7	90	48	0.06	35.50	15.70
8	110	48	0.06	78.00	58.20

According to results, the optimum parameters to produce the highest yield of zeolite (on average 78%) are reaction temperature of 110°C and reaction time of 48 hours with loading of reactants of 0.06. The factors effect under the specified parameters is 58.2% higher than in reference parameters. It should be noted that the effect of reaction duration is also essential, as parameter set No. 3 reveals the third highest yield of zeolite; thus it could be expected that zeolite formation directly proportional to reaction time. In this case, the factors effect is 28.45%, which is 7.65% lower than in No. 6. The conditions (factors) applied in experiment No. 8 was used for all other synthesis of zeolites.

3.2. Mineralogical characterization of zeolites

The phase content of synthetic zeolites produced from CFA varies depending on the origin of raw material and reaction conditions. figures 1-2 show the XRD spectrum of synthetic zeolites produced from two different Kazakhstani CFAs.

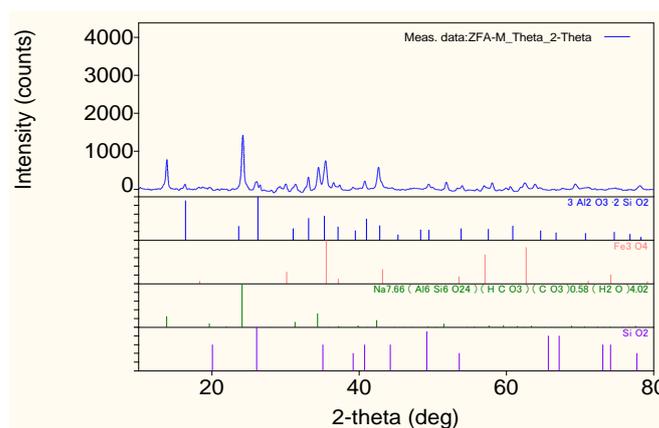


Figure 1. XRD spectrum of M-ZFA.

In general, all zeolites contain phases as mullite, quartz and magnetite/hematite (variations of iron oxides), which are the main phases of parent CFAs. The semi-quantitative tool of software allows identification of the crystalline phases in percentage. The calculation reveals that the content of crystalline mullite and quartz in both ZFAs is negligible. It should be noted that the amount of

magnetite/hematite present in CFAs was not detected on this instrument because it is mostly amorphous and only crystalline particles of this phase was used in percentile calculation of software.

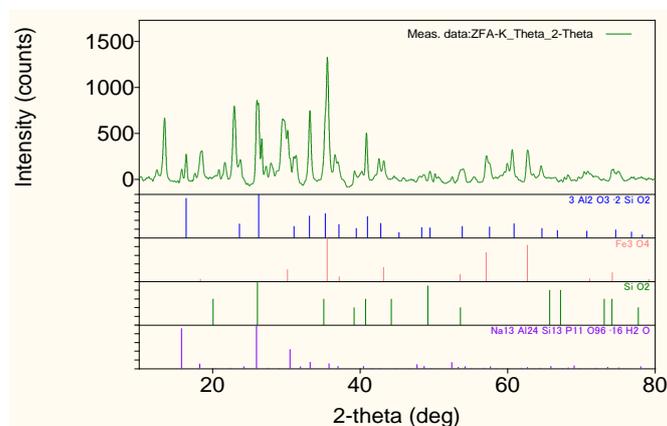


Figure 2. XRD spectrum of K-ZFA.

The detailed chemical composition of K-ZFA and M-ZFA is shown in table 3. According to data the main chemical elements in ZFAs are Al, Si, Fe and Ca, as expected.

Table 3. Elemental composition of Kazakhstani ZFAs.

Compound	K-ZFA	M-ZFA
Na ₂ O	4.447	5.858
MgO	0.708	1.145
Al ₂ O ₃	30.888	24.859
SiO ₂	32.488	32.343
SO ₃	0.086	0.874
Cl	0.030	0.023
K ₂ O	0.150	0.260
CaO	2.390	4.696
TiO ₂	1.258	0.959
Cr ₂ O ₃	3.104	3.387
MnO	0.411	0.608
Fe ₂ O ₃	23.066	23.578
CuO	0.028	0.034
ZnO	0.040	0.036
Co ₃ O ₄	0.061	0.070
SrO	0.206	0.309
Y ₂ O ₃	0.013	0.009
ZrO ₂	0.074	0.051
BaO	0.119	0.273

However, it is apparent that the content of iron oxide is comparatively lower in K-ZFA (23.066%) in contrast with M-ZFA (23.578%) and noticeably higher than in ZFAs produced from CFAs of other regions of the world [4-10]. It is interesting to note that K-ZFA contain 2 times lower amount of CaO (2.390 and 2.512 wt.%) than in M-ZFA (4.696 wt.%). The total amount of alkaline oxides are relatively higher in M-ZFA (11.959 wt.%) that in turn results in more basic properties. Both ZFAs contain trace amount of heavy metals with concentrations below 0.1wt.% (Co, Cu, Zn, Ga, Sr, Y and Zr). The Si/Al ratio of K-ZFA and M-ZFA are 0.93 and 1.15, respectively. The results are comparable with data published elsewhere [20, 31].

3.3. Microstructural characterization of zeolites

The most characteristic property of all zeolitic materials is their porosity. The general porosimetric analysis using inert gas (argon or nitrogen) could give the porosity type, the SSA, total volume of pores, average pore size.

Table 4 summarizes the experimental results obtained for both ZFAs samples by applying three different adsorption models (isotherms), namely BET, BJH and DFT. It should be noted that the BET method is used for comparison with literature values, as this approach is commonly applied for porosimetric analysis of porous materials.

According to the results obtained by BET method, K-ZFA is the most porous zeolite, where it reveals the average pore diameter of 14.642 nm with the SSA value of 67.734 m²/g. The total pore volume for pores less than 376.4 nm is 0.248 cm³/g. This is followed by M-ZFA that demonstrate a wider pore size of 20.104 nm and SSA value of almost 10 m²/g lower than in K-ZFA. The total pore volume, on the other hand, is about the same as in K-ZFA and reveals the value of 0.291 cm³/g. In comparison with zeolites, the SSAs of K-CFA and M-ZFA are 32.873 m²/g and 12.734 m²/g, respectively.

Table 4. Porosimetric analysis of Kazakhstani ZFAs.

ZFA type	Average pore diameter [nm]	Specific surface area [m ² /g]	Total pore volume [cm ³ /g]
K-ZFA	14.642 (BET)	67.734 (BET)	0.248 (BET)
	4.367 (DFT)	46.608 (DFT)	0.138 (DFT)
	3.706 (BJH)	69.253 (BJH)	0.183 (BJH)
M-ZFA	20.104 (BET)	58.191 (BET)	0.291 (BET)
	4.520 (DFT)	62.562 (DFT)	0.179 (DFT)
	3.918 (BJH)	98.052 (BJH)	0.234 (BJH)

According to the results of particle size analysis shown in table 5, K-ZFA and M-ZFA demonstrate similar distribution in terms of average particle size distribution at 26.30 μm and 29.30 μm, respectively. As for particles less than 10% they reveal 6.01 μm (K-ZFA) and 9.26 μm (M-ZFA); while 90% of particle size for these two ZFAs ranges between 66-191 μm.

Table 5. Particle size analysis of ZFAs.

CFA type	Uniformity	Dv(10), μm	Dv(50), μm	Dv(90), μm
K-ZFA	0.711	6.01	26.30	66.60
M-ZFA	1.807	9.26	29.30	191.00

3.4. Batch adsorption studies

The produced zeolites, namely K-ZFA and M-ZFA and their parent CFAs, were tested for adsorption capacity of mercury (II) ions from aqueous solutions with initial Hg(II) ions concentration of 10 ppm under acidic conditions (pH = 2) to avoid precipitation. In total the equilibrium for ZFAs reached after 336 hours or 14 days, while for CFA in reached after 696 hours or 29 days. The results of the adsorption studies is presented in figure 3.

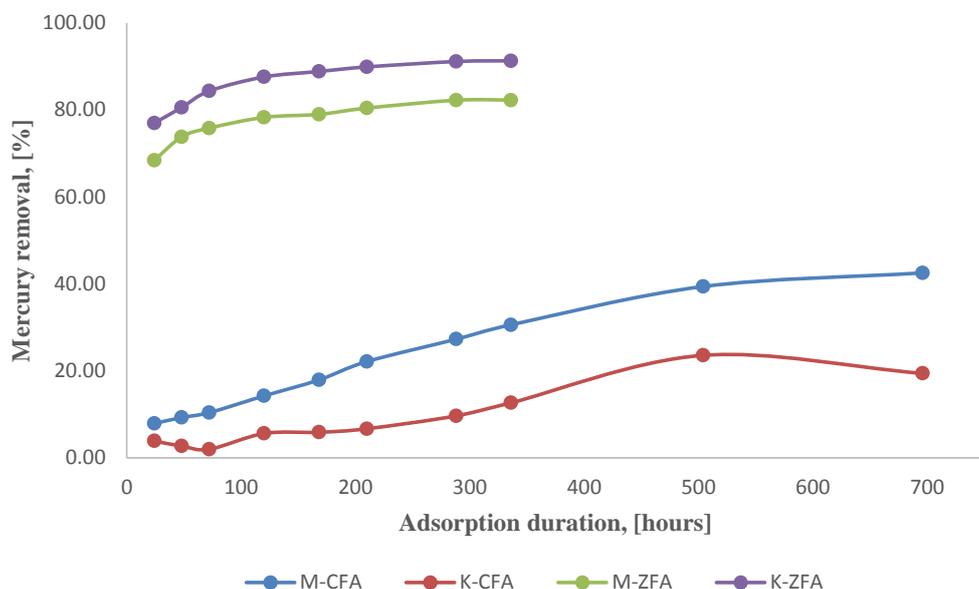


Figure 3. Mercury removal studies of ZFAs.

As it is seen from figure 3, both ZFAs demonstrate significantly higher removal than their respective parent CFAs: K-ZFA removed 91.27% of Hg(II) ions, whereas K-CFA removed 19.43% of Hg (II) ions. On the other hand, M-ZFA demonstrated slightly lower removal of 82.23% Hg (II) ions, while parent M-CFA showed 42.53% that is almost twice as lower as in zeolite. A minor adsorption of Hg (II) ions on container walls and/or evaporation resulted from reduction to Hg (0) was observed during experimental studies. These values were subtracted from obtained values to provide with comparable calculated data.

4. Conclusion

ZFAs produced under optimum reaction conditions were characterized for mineralogy and microstructure and tested for removal efficiency for mercury (II) ions from aqueous phase. The advanced methods, such as XRD, XRF, PSA and porosimetric analysis were successfully applied to obtain valuable characteristic data on these Kazakhstani ZFAs. It was identified that both ZFAs contain mullite, quartz and magnetite/hematite as a residual from parent CFAs, while the major phase being sodalite for M-ZFA and analcime for K-ZFA. The main elements that present in zeolites are Si, Al, Fe, Mn and alkaline metals. Porosimetric analysis revealed that the BET surface area of K-ZFA and M-ZFA are 67.734 m²/g and 58.191 m²/g, respectively. The average pore diameter reveals that both ZFAs have mesoporous structure. The results of particle size analysis showed that 50% of particles are less than 26.30-29.30 μm.

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