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Zeolite development from fly ash and utilization in lignite mine-water treatment

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ABSTRACT

Fly ash from two lignite-fed power stations in Greece (Megalopolis and Meliti) has been utilized to synthesize zeolitic materials with upgraded adsorption capacity. Two different siliceous fly ash samples were subjected to hydrothermal treatment at fixed solid/liquid ratio and constant temperature. The zeolitic products have been characterized for their microstructure, chemical, and mineralogical composition by means of SEM, AAS, and XRD, respectively. The primary zeolitic crystals identified were phillipsite and thomsonite, in Megalopolis and Meliti fly ash, respectively. In light of their prospective utilization as liquid-phase sorbents, the specific surface area and porosity of materials were also determined, by means of N_2-porosimetry. The zeolitic samples were tested for their actual heavy metal-removal capacity by water sampled from active lignite mines in Northern Greece. Artificial aquatic samples with known concentration of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) were also tested, showing that the synthetic zeolitic materials are good to uptake a wide variety of potential pollutants with up to 100% efficiency. The efficiency of the synthetic zeolitic materials was comparatively assessed, showing that the more intense the presence of phillipsite in the synthetic materials, the greater the uptake rates for certain groups of trace elements.

1. Introduction

Particular properties of zeolites, such as high cation exchange capacity (CEC) and porous structure, render them suitable materials for a variety of industrial applications. The high Al^{3+}/Si^{4+} ratio of some types of zeolites accounts for the high CEC (up to 5 meq/g) of some zeolites such as A, NaP1, X, KM, F, chabazite and herschelite. For these reasons, the heavy metals and ammonium uptake have been the major application field tested, while the use of synthetic zeolites as molecular sieves for gas cleaning technologies, including CO_2 sorption, has been also investigated (Querol et al., 2001; Juan et al., 2009; Olivares-Marín et al., 2010).

The synthesis of zeolites from fly ash was prompted by Holler and Wrisching (1985) due to the compositional similarity of these products to some volcanic materials, precursor of natural zeolites. Afterwards, many patents and technical articles have proposed different methods to synthesize different types of zeolites from fly ash (FA). Most of these methodologies are based on the alkaline hydrothermal activation (by NaOH and KOH) (Sommerville et al., 2013; Murayama et al., 2002; Derkowski et al., 2007; Murayama et al., 2008; Majchrzak-Kucęba and Nowak, 2011). Shigemoto et al. (1992) optimised the traditional direct conversion method by the introduction of a fusion step prior to synthesis. This fact permitted to obtain different types of zeolites with potential industrial application (such as NaP1, chabazite, herschelite). The direct conversion method was also applied by the use of dry conversion systems (Park et al., 2000). Other studies on direct conversion allowed reducing the synthesis time (from hours to few minutes) by microwave-assisted method (Querol et al., 1997a). However, the zeolitic products obtained by direct conversion have relatively low CEC values due mainly to incomplete conversion of the fly ash in zeolite. Hollman et al. (1999) prompted the synthesis of zeolites from SiO_2 extracts from FAs obtaining high purity zeolites (>95% of A and X zeolite), and Moreno et al. (2002) optimised this method synthesizing in the same process zeolites with high purity from SiO_2 extracts and another zeolitic product (the solid residue from SiO_2 extracts), equivalent to zeolites obtained by direct conversion method. Alkaline fusion process was also tested and improved to obtain high porous size and CEC zeolitic material (Moreno et al., 2001).

The safe and cost-effective management of toxic metal-containing wastewater remains a challenging task for industrialists and environmentalists. The traditional treatment methods of heavy metal (HM)-contaminated aquatic discharges, such as reduction precipitation, ion exchange, electrochemical reduction, and reverse osmosis, involve large exposed liquid surface area and long detention periods as well as high capital cost, rendering effective low-cost adsorbents such as fly ash-based zeolites absolutely necessary for numerous industrial sectors

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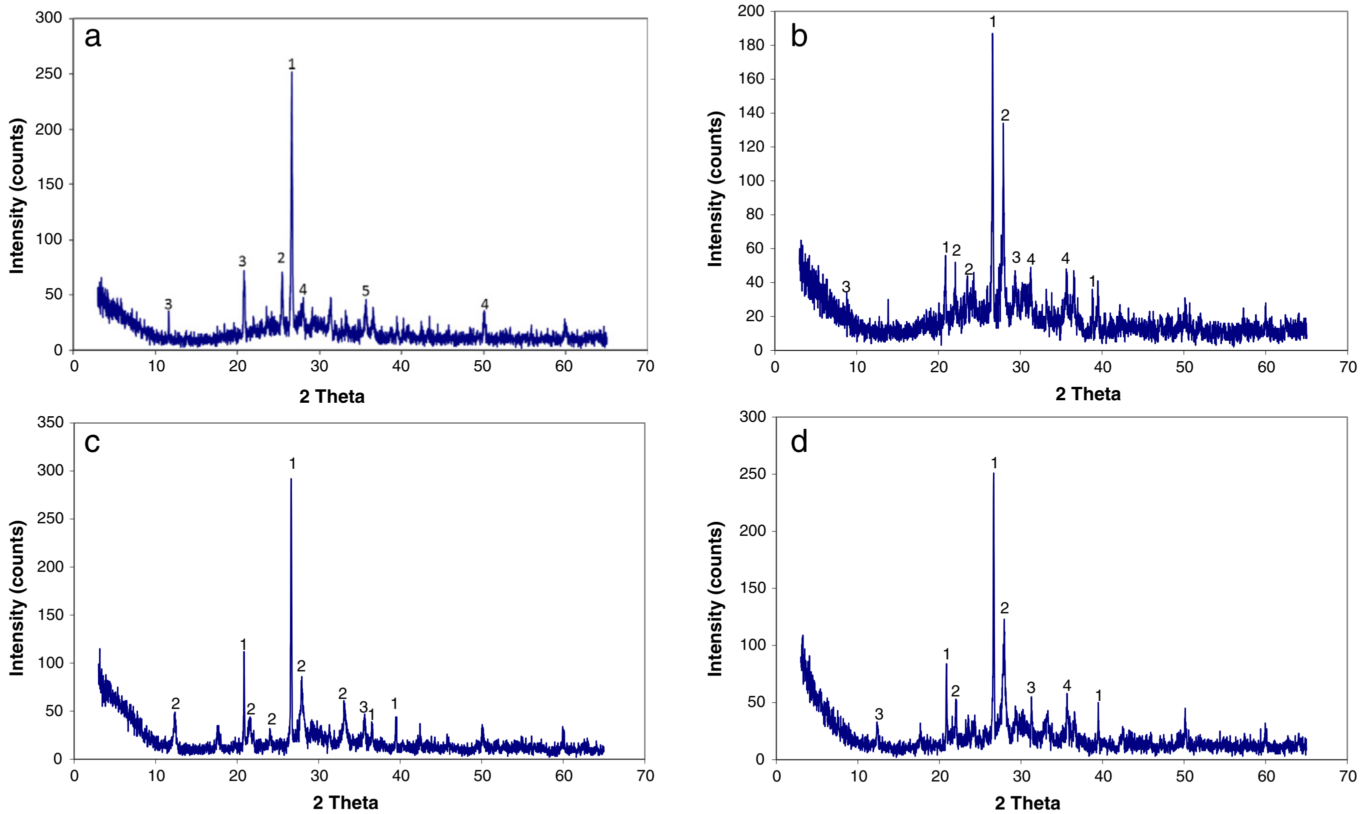

Fig. 1. a X-Ray diffractogram, Megalopolis fly ash. 1: quartz; 2: anhydrite; 3: gypsum; 4: albite; 5: hematite. b X-Ray diffractogram, Meliti fly ash. 1: quartz; 2: albite; 3: muscovite; 4: hematite. c X-Ray diffractogram, MG-FA-based zeolitic material. 1: quartz; 2: phillipsite; 3: hematite. d X-Ray diffractogram, MT-FA-based zeolitic material. 1: quartz; 2: albite; 3: thomsonite; 4: hematite.

(Godfrey et al., 2010; Rao et al., 2002). The main driver behind this study was to extend the ash/zeolite applications to mine wastewater treatment, especially focusing on coal mine-water, due to the proximity of such sites with coal power plants and the subsequent low transportation cost it entails. It is noted that the transportation – and consequently the production – cost of ash-based zeolites is the main barrier to their industrial-scale synthesis and utilization (as vast quantities of fly ash have to be transported from the thermal power plant to the zeolitization plant, and thermal power stations are not always ideally located to introduce a market-oriented product focusing on small-medium environmental enterprises). The experimental work included zeolite synthesis from fly ash collected by two Hellenic thermal power stations, i.e. Megalopolis and Meliti, in Southern and Northern Greece, respectively. Both plants are normally fed by the nearby lignite mines. This is the first attempt to produce zeolites from Meliti fly ash, a relatively new power station (operates since 2003), which normally produces siliceous fly ash but the quality may vary greatly from time to time due to feedcoal inhomogeneity. It is also the first attempt (to the best of the authors' knowledge) to use the fly ash-based product in an aqueous environment that is closely located to the thermal power plant that produces it. The most representative samples of a rather prolonged operation period have been collected, mixed together, analysed and further processed to synthesize the zeolitic products.

2. Materials and methods

2.1. Fly ash sampling and zeolitization

Representative fly ash (FA) samples have been collected from the electrostatic precipitators of two different lignite-fired power plants of Greece (Megalopolis (Southern Greece) (850 MW) and Meliti (Florina, Northern Greece) (330 MW) thermal power stations), under maximum electricity load (hereinafter referred to as MG-FA and MT-FA, respectively). MG-FA and MT-FA samples underwent alkaline hydrothermal treatment at 90 °C, using 1 L NaOH 1 M per 50 g FA. The incubation period was set at 24 h and the mixing took place at 150 rounds per minute (rpm). After that period, the mixture was filtered and the solid residue was dried at 40 °C for 24 h and leached with water until no NaOH was detected.

2.2. Material characterization

The determination of major element concentration of MG- and MT-FAs and zeolitic products was performed by Flame Atomic Absorption Spectroscopy (FAAS). The mineralogy of FAs and the synthetic zeolitic materials was examined by X-Ray Diffraction (XRD) using a Bruker D-8 ADVANCE instrument, while their microstructure has been investigated by means of Scanning Electron Microscopy (SEM, 6300 JEOL). The chemical composition of particularly selected areas of sorbents was determined by means of Energy-Dispersive X-Ray Spectroscopy (EDS) using an automated analysis system, installed on the SEM instrument. The specific surface area and porosity of both the FA samples and the

Table 1
Chemical composition (wt.%) of Megalopolis and Meliti fly ash.

Compound (%)	MG-FA	MT-FA
SiO_2	49.2	55.12
Al_2O_3	19.9	17.3
Fe_2O_3	7.0	6.84
CaO	12.48	11.9
MgO	2.92	3.01
K_2O	2.66	1.86
Na_2O	1.86	0.7
SO_3	2.8	2.91