



Research article

Removal of heavy metals from wastewater using CFB-coal fly ash zeolitic materials

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ARTICLE INFO

Article history:

Received 16 June 2009

Received in revised form 24 August 2009

Accepted 26 August 2009

Available online 31 August 2009

Keywords:

CFB

Coal fly ash

Synthetic zeolites

Water treatment

Heavy metals

ABSTRACT

Polish bituminous (PB) and South African (SA) coal fly ash (FA) samples, derived from pilot-scale circulated fluidized bed (CFB) combustion facilities, were utilized as raw materials for the synthesis of zeolitic products. The two FAs underwent a hydrothermal activation with 1 M NaOH solution. Two different FA/NaOH solution/ratios (50, 100 g/L) were applied for each sample and several zeolitic materials were formed. The experimental products were characterized by means of X-ray diffraction (XRD) and energy dispersive X-ray coupled-scanning electron microscope (EDX/SEM), while X-ray fluorescence (XRF) was applied for the determination of their chemical composition. The zeolitic products were also evaluated in terms of their cation exchange capacity (CEC), specific surface area (SSA), specific gravity (SG), particle size distribution (PSD), pH and the range of their micro- and macroporosity. Afterwards the hybrid materials were tested for their ability of adsorbing Cr, Pb, Ni, Cu, Cd and Zn from contaminated liquids. Main parameters for the precipitation of the heavy metals, as it was concluded from the experimental results, are the mineralogical composition of the initial fly ashes, as well as the type and the amount of the produced zeolite and specifically the mechanism by which the metals ions are hold on the substrate.

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1. Introduction

The combustion of solid fuels using conventional technologies dominates the coal-burning power production. However, more environmental-friendly technologies, such as the CFB combustion technology, continuously gain ground. Therefore, the amounts of CFB-derived coal fly ash, are steadily increasing, as a result of the continuous development of the CFB technologies [1]. It is obvious that alternative applications should be developed in order to recycle the high FA output [2]. The production of zeolites is one of the potential applications of fly ash in order to obtain high value industrial products with environmental technology utilization. The synthesis of zeolite products from fly ash is analogous to the formation of natural zeolites from volcanic deposits or other high-Si–Al materials [3,4]. Both volcanic ash and FA are fine-grained and contain a large amount of active aluminosilicate glass. One of the processes from which zeolites can be naturally formed is through the influence of hot groundwater on the glass fraction of volcanic ash. The particular zeolitic development may take thousands of

years in order to form natural zeolites. In the laboratory the process can be speeded up (to days or hours) for both volcanic ash and FA. In that case the activation solution is an alkaline one, usually NaOH or KOH. The classical alkaline conversion of fly ash is based on the combination of different activation solution/FA ratios, with temperature, pressure and reaction time to obtain different zeolitic types. The methodologies developed on this field aim at the dissolution of Al–Si bearing phases of the FA and the subsequent precipitation of the zeolitic material [5,6]. NaOH or KOH solutions with different molarities, at atmospheric and water vapor pressure, from 80 to 200 °C and 3 to 96 h have been combined to synthesize many different types of zeolites. The zeolitic content of the resulting products varies depending on the solution/fly ash ratio applied and on their reaction time [7]. All the aforementioned procedures utilize coal fly ash from conventional combustion and very little research has been conducted on the field of CFB-derived coal FA utilization. The present study deals with the hydrothermal activation of two coal FAs produced in pilot-scale CFB combustion facilities and aims at testing the synthetic products for their potential to be used as low-cost adsorbents for the removal of heavy metals from industrial wastewater. The traditional treatment methods of the heavy-metal contaminated aquatic environments, such as the reduction precipitation, the ion exchange, the electrochemical reduction, the reverse osmosis, etc., are methods that involve large exposed liquid sur-

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Table 1
The effect of alkaline hydrothermal activation on the composition of the major chemical compounds of CFB-fly ashes.

Compound	Before hydrothermal activation		After hydrothermal activation			
	PB-FA	SA-FA	PB-FA (50 g/L)	PB-FA (100 g/L)	SA-FA (50 g/L)	SA-FA (100 g/L)
SiO ₂	38.99	48.94	29.43	30.35	37.03	36.82
Al ₂ O ₃	25.39	34.71	12.59	14.14	20.58	20.87
Na ₂ O	1.70	0.35	6.43	4.18	9.71	9.52
SO ₃	8.82	5.59	0.96	0.80	0.43	0.66
CaO	17.54	10.12	20.61	20.33	11.95	11.75

face area and long detention periods as well as high capital cost, usually not-affordable for small-scale industries. Thus, the cost-effective disposal of heavy metal-containing wastewater remains a challenging task for industrialists and environmentalists [8,9].

2. Materials and methods

PB-FA and SA-FA derived from CFB facilities underwent an alkaline hydrothermal treatment at 90 °C, using NaOH 1 M as an activation solution, in a 1 L stainless steel reactor. The incubation period was set at 24 h and 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. Chemical analyses of PB- and SA-CFB-FAs as raw material as well as zeolitic products were performed by X-ray fluorescence (XRF). The mineralogical composition of the zeolitic materials was identified by X-ray diffraction (XRD) and scanning electron microscope (SEM). The synthetic zeolitic materials were subjected to N₂ adsorption using BET method in order to determine their specific surface area (SSA), while their cation exchange capacity (CEC) was evaluated following the US EPA 9081 method (sodium acetate). The particle size distribution (PSD) of the initial FAs and the synthesized zeolitic materials was determined by Malvern Mastersizer-S using the wet dispersion method in water. The study of the range of macro- and microporosity in the synthetic zeolitic materials was performed using a porosimeter Autosorb-1 (with crypton analysis, optimum for microporosity) made by Quanta-Chrome. Furthermore, the pH (ISO 6588) and the specific gravity (SG-ASTM C642) of the initial FAs and the synthetic zeolitic materials were also evaluated. In order to test the synthetic zeolitic materials for their capability of removing heavy metals from wastewater, an aqueous solution of 1000 mg/L (each) of Cr, Cu, Ni, Pb, Zn and 100 mg/L Cd was prepared. The procedure involved filling a series of glass tubes with 50 mL of solution, adding 10 g of adsorbent to them and then implementing mechanical stirring at 200 rpm. Although the incubation period was set at 24 h, the preliminary investigations showed that the uptake of all the examined metals, by all the zeolitic materials, was completed within 2 h, since

Table 2
Mineralogical phases identified in the synthetic zeolitic materials (+: presence of mineral phase, -: absence of mineral phase).

Mineral	PB-FA (50 g/L)	PB-FA (100 g/L)	SA-FA (50 g/L)	SA-FA (100 g/L)
Quartz	+	+	+	+
Calcite	+	+	+	+
Magadiite	+	+	–	–
Lime	+	+	–	–
Hematite	+	+	+	+
Portlandite	+	+	+	+
Illite	+	+	–	–
Zeolite A (Na)	–	–	+	+
Zeolite A (K)	–	–	+	+
Unnamed Zeolite	+	+	–	–
ZSM-18	+	+	–	–
Linde (L)	–	+	–	–
Erionite	+	+	+	–

no practical change was detected up to the period of 24 h. Afterwards, the supernatant solution was filtered and subjected to flame atomic adsorption spectroscopy (FAAS). The process was repeated for three times and the average measured values are given as the final results of the (%) heavy-metal uptake by the zeolitic materials. The standard deviation for the uptake of metals lies within a small range: presents a minimum in the case of Ni (0.01%) and reaches a maximum on the occasion of Cr (0.025%)

3. Results and discussion

3.1. Synthetic procedure of zeolitic materials and their characterization

3.1.1. Chemical composition

NaOH (1 M) solution was selected as activation solution, since it presents higher conversion efficiency than KOH, under the same temperature. The experimental conditions (NaOH concentration, temperature) are typical for pure alkaline activation, taking place at low temperatures and intermediate activation periods [10,11,12]. The applied techniques mainly aim at the dissolution of Al–Si bearing phases of FA and the subsequent precipitation of the zeolitic materials. Table 1 illustrates the impact of the alkaline activation on the chemical composition of the raw materials (CFB-fly ashes), which is profound concerning the analogous reduction in the percentages of SiO₂ and Al₂O₃. The effect of NaOH on the alumino-silicate materials is tremendously intense, mainly because of the presence of aluminum. In fact, it causes differentiation in the distribution of the electric charge between the Al–O and Si–O bonds that results in the polarization of the chemical bonds and the enhancement of the chemically active centres (of positive and negative charge) in the lattice. Thus, terminal groups such as ≡Si–OH, ≡Si–ONa, ≡Si–O–, (≡Si–O)3Al–O– are developed and, along with NaOH, lead to the formation of more complex products (i.e. zeolites) [13–16]. Therefore, NaOH solutions present higher conversion efficiency than the respective KOH under the same temperature, as it is also concluded from the vast body [3–8,10–12] of previous research studies.

3.1.2. Mineralogical composition and microstructure

The final solid products were subjected to mineralogical analysis for the identification of known zeolites. The results are presented in Table 2; in this table there can also be found the rest identified phases that are attributed to the initial fly ashes. The formation of the aforementioned zeolitic products was also confirmed by SEM investigation (Figs. 1–6). In Figs. 1 and 2 the zeolitic grains of PB-FA treated samples (included in Table 2) can be clearly observed. Figs. 3–6 include the SEM photos of the alkaline-treated SA-FA (50 and 100 g/L FA/NaOH ratios), where the cubic structures refer to Zeolite-A. That fact was confirmed after examining the chemical composition of the synthetic zeolitic materials in respect with their microstructural formation by means of EDAX-coupled SEM (Figs. 7–10).

Fig. 7 presents a cluster of cubic zeolitic crystals of the hybrid product formed after the treatment of SA-FA. It is clear, from

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