



Review

Fly ash zeolites for water treatment applications

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ARTICLE INFO

Article history:

Received 8 November 2015

Received in revised form 8 January 2016

Accepted 1 February 2016

Available online 2 February 2016

Keywords:

Fly ash zeolite

Applications

Water treatment

Heavy metal removal

Effluent treatment

Permeable reactive barrier

ABSTRACT

In the last few decades, fly ash, a coal combustion residue, has been used as a raw material for synthesis of microporous aluminosiliceous minerals known as zeolites. Due to their excellent ion exchange capacity, high surface area and unique pore characteristics, zeolites have been used for removal of heavy metals (viz., As, Cd, Cr, Cs, Cu, Fe, Hg, Mn, Ni, Pb, Sr, W and Zn) and ionic species (viz., ammonium, chloride, fluoride, nitrate, phosphate and sulphate) from industrial sludges, acid mine drainage and wastewater from domestic and industrial sources. In addition, fly ash zeolites find their application as sorbent medium in permeable reactive barriers and contaminant barrier liners for immobilizing the contaminant plume in soil. This paper reviews the applications of fly ash zeolites in various water treatment studies and other related environmental cleanup projects, viz., depuration of wastewater containing industrial dyes and hazardous ions and leachate treatment. Furthermore, novel applications in the use of fly ash zeolites as permeable reactive barriers and contaminant barrier liners as well as the future scope of research for environmental cleanup are also discussed.

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1. Introduction

Fly ash is a coal combustion by-product generated in large quantities from coal thermal power plants around the globe [23]. Hence, its utilization has gained momentum in the past few decades and has been used as cement additive (due to its pozzolanic property), in brick manufacturing [98], as backfill material [125,152], for reinforcing filler in polymers [100,60] and as

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Nomenclature

Notation

AMD	Acid mine drainage
BOD	Biological oxygen demand
CEC	Cation exchange capacity (in meq/100 g)
c_e	Equilibrium concentration (in mg/l)
c_i	Initial ion concentration (in mg/l)
COD	Chemical oxygen demand
HTAB	Hexadecyltrimethylammonium bromide
pH _e	pH after interaction
PRB	Permeable reactive barrier
PZC	Point of zero charge
q	Contaminant uptake (in mg/g)
SSA	Specific surface area (in m ² /g)
t	Interaction time
T	Temperature (in °C)
VOC	Volatile organic compounds
η	Contaminant removal efficiency (in %)

a soil ameliorant [82]. Furthermore, due to its high silica and alumina content, fly ash has been perceived as an ideal precursor for synthesis of zeolites [69] and geopolymers [154,39].

Zeolites are three-dimensional tetrahedral aluminosilicate minerals, having their negative charge (generated by isomorphous substitution of Si⁴⁺ by Al³⁺) counterbalanced by native cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) and water molecules in their pores and channels. The general formula for a zeolite is M_{2/n}O·Al₂O₃·xSiO₂·yH₂O where M is any alkali or alkaline earth element, n is the valence charge on that element, x varies from 2 to 10 and y varies from 2 to 7. The Al₂O₃ and SiO₂ are the structural cations because they form the tetrahedral framework with oxygen [120]. Some common zeolites synthesized from fly ash are presented in Table 1. Naturally occurring zeolites (natural zeolites) have restricted pore sizes and channels, whereas fly ash-based synthetic zeolites possess a variety of pore structures and are potential and probably economically viable sorbent minerals for trapping various contaminants from air and water [70,56]. Though raw fly ash has the potential for the removal of heavy metals, dyes and anions [115,172,33,62,10,109,17,11], zeolites synthesized from it, augment its immobilization characteristics to several folds [107,173,105]. Incidentally, zeolitized fly ash has been reported to have higher lead sorption capacity than raw fly ash (6–7 times) and natural zeolites (3–5 times) [104,78].

Table 1
Some common zeolites synthesized from fly ash.

Zeolite	Chemical formula	References
Analcime	NaAlSi ₂ O ₆ ·H ₂ O	[146]
Cancrinite	Na ₆ Ca ₂ Al ₆ Si ₆ O ₂₄ (CO ₃) ₂ ·2H ₂ O	[138]
Chabazite	(Ca,Na ₂ ,K ₂ ,Mg)Al ₂ Si ₄ O ₁₂ ·6H ₂ O	[43]
Clinoptilolite	(Na,K,Ca) ₂₋₃ Al ₃ (Al,Si) ₂ Si ₁₃ O ₃₆ ·12H ₂ O	[178]
Hydroxy-sodalite	Na _{1.08} Al ₂ Si _{1.68} O _{7.44} ·1.8H ₂ O	[2]
Mordenite	(Ca, Na ₂ , K ₂)Al ₂ Si ₁₀ O ₂₄ ·7H ₂ O	[150]
Na-A	Na ₁₂ Al ₁₂ Si ₁₂ O ₄₈ ·24H ₂ O	[138]
Na-P1	Na ₆ Al ₄ Si ₄ O ₂₄ ·4H ₂ O	[138]
Na-Y	Na ₅₈ Al ₅₈ Si ₁₃₄ O ₃₈₄ ·260H ₂ O	[138]
Scolecite	Ca ₂ Al ₂ Si ₃ O ₁₀ ·3H ₂ O	[138]
Phillipsite	(Ca,Na ₂ ,K ₂) ₃ Al ₆ Si ₁₀ O ₃₂ ·12H ₂ O	[67]
Zeolite A	NaAlSi _{1.1} O _{4.2} ·2.25H ₂ O	[2]
Zeolite X	NaAlSi _{1.23} O _{4.46} ·3.07H ₂ O	[2]
Zeolite Y	NaAlSi _{2.43} O _{6.86} ·4.46H ₂ O	[2]

Utilization of fly ash for synthesizing zeolites and determination of their heavy metal uptake potential is important in consumption of ash currently dumped at disposal sites and also for creating water treatment solutions for regions/countries facing limited water resources. Based on the available literature, the locations of fly ashes, which have been zeolitized for applications in depuration of contaminated water and wastewater, have been illustrated in Fig. 1. In spite of India producing over 130 million tons/year and Russia having 1.5 billion tons of ash-slag waste stored in ash-disposal sites, very few studies have been conducted in these countries with regard to environmental cleanup using fly ash zeolites that would subsequently help in the bulk utilization of fly ash [66,89,113,74,136].

1.1. Synthesis and pretreatment of zeolites before their applications

Fly ash due to its activation using alkalis, such as NaOH, KOH, Ca(OH)₂ and LiOH, undergoes dissolution and subsequently crystallizes into zeolitic minerals [157,94,117,31,112,84,95,96]. The synthesis methods include: (i) conventional hydrothermal treatment [69,121,1,37,118,45]; [54]; [169], (ii) alkali fusion-assisted hydrothermal treatment [151,127,161,114,174,91,83], (iii) microwave-assisted hydrothermal treatment [76,139,160], (iv) ultrasonication-assisted hydrothermal [55,13,92,20,18] and (v) molten salt method [131,34]. In addition, pure zeolites can be synthesized from silica and alumina extracts obtained by alkali leaching of fly ash [51]. Upon activation, the particle size range of the original fly ash (generally, 0.5 μm to 400 μm) decreases, due to the alkali etching on the surface of the fly ash particles and subsequent nucleation and crystallization of small zeolitic minerals (Fig. 2), finally resulting in an increase in specific surface area [14,163,80]. Consequently, this augmentation in surface area facilitates better sorption characteristics in the end product (read zeolites).

The presence of significant amount of fly ash residues after synthesis of zeolites limits its contaminant sorption capacity [180]. Hence, pretreatment of raw fly ash can be employed to obtain purer zeolites as well as for synthesizing application-specific end products. In larger particle size fractions of fly ash, i.e., >250 μm, unburnt carbon is also present (generally, less than 20% depending on type of coal and coal-firing system), which can be removed using sieves in order to increase its zeolitization potential, resulting in a larger surface area [86,79,164,27]. Alternatively, calcination at elevated temperature (800 °C) can remove unburned carbon and other volatile compounds [135]. Furthermore, the removal of Fe₂O₃ and TiO₂ using magnetic separation also enhances the zeolitic end products in terms of its purity and structure [104,27]. A 6000 Gauss permanent magnet coated with a low-porosity paper can be used to manually separate the magnetic and non-magnetic fractions [27]. Interestingly, surface loading on zeolites with species such as iron and titanium, has been reported to boost their cation exchange capacity [46,47,165]. Washing of fly ash with water reduces the concentration of soluble compounds such as Na₂O, MgO, CaO and K₂O [166,164] and lowers the pH (which is initially >10) [122]. In addition, acid treatment removes impurities, such as iron oxide, from raw fly ash, yielding a higher concentration of aluminosilicates [166,183]. Furthermore, the synthesized zeolites can be washed with NaCl solution to obtain mono-cation saturated zeolite (i.e., sodium zeolite), which offers better ion exchange capacity [171,181]. In this context, although washing using distilled/deionized water lowers the pH, the pH of synthesized zeolite is generally not lowered below neutral [85]. This is because drastic lowering of pH can cause collapse of the zeolitic crystals, which is initially indicated by exfoliation of top layers of crystals (at pH 4.2 for zeolite P), followed by entire breakdown of crystallinity (at pH 3.8 for zeolite P) and subsequent exposure of the underlying fly ash spherules [122,137]. In addition,

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