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A REVIEW ON CHARACTERIZATION AND APPLICATION OF FLY ASH ZEOLITES

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ABSTRACT

zeolites are aluminosiliceous minerals which are well-known for their porous crystal structures and chemical characteristics. Due to these capabilities, researchers have synthesized zeolites from substances containing alumina and silica, viz. kaolin, sediments, etc. In this context, fly ash has been perceived to be a prospective raw material for zeolitization since it can undergo geopolymerisation in an alkaline medium at specific conditions of temperature and pressure. Since several decades, naturally occurring zeolites have been used for animal husbandry and agri- and aqua-culture. Furthermore, due to their hollow cage-like structure, they are also being used as molecular sieves, ion-exchangers and catalysts. Moreover, their remarkable cation-exchange capacity, CEC, enables them to be used as an additive to fertilizers so as to increase the nutrient retention capacity of the soil thereby increasing the fertility of the land and boosting the crop yield. Being an agrarian nation, the Indian economy would be greatly affected by enhanced fertility of the land following a cost-effective manner of nutrient addition and retention, wherein fly ash based zeolites would play a very significant and crucial role. This is also due to the inherent nature of the zeolites, which makes them an excellent 'sorbent' which helps cleaning up of the polluted soils and water bodies. Also, the sorption characteristics of zeolites can also be employed for removal of ammonia from the waste water.This calls for development of appropriate process for large-scale industrial production of the ash based zeolites, exhibiting high CEC value, for their utilization in various walks of the society (viz., environmental clean-up activities) It is believed that opportunely synthesized zeolites could become a panacea for sustainable development.

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INTRODUCTION

Generation of electricity by combustion of coal in thermal power plants releases a colossal amount of fly ash as the major by-product which is usually dumped into the lagoons, thereby consuming valuable land area. Consequently, there has been a wide interest in using it for various purposes such as land reclamation, soft soil stabilisation, manufacture of bricks, cement, acidic waste scrubber, carbon nanotubes, etc. Apart from these conventional applications, fly ash has also been employed to synthesize zeolites, which owing to their high silica and alumina contents.

Primarily, zeolites are aluminosiliceous minerals which are well-known for their porous crystal structures and chemical characteristics. Due to these capabilities, researchers have synthesized zeolites from substances containing alumina and silica, viz. kaolin, sediments, etc. In this context, fly ash has been perceived to be a prospective raw material for zeolitization since it can undergo geopolymerisation in an alkaline medium at specific conditions of temperature and pressure. Consequently, several synthesis methods have been proposed by varying the reaction conditions (viz., pH, Si/Al ratio, type of reaction and interaction time) and reactants (viz., NaOH, KOH, Na_2CO_3, $Ca(OH)_2$, NH_4F, etc).

Since several decades, naturally occurring zeolites have been used for animal husbandry and agri- and aqua-culture. Furthermore, due to their hollow cage-like structure, they are also being used as molecular sieves, ion-exchangers and catalysts. Moreover, their remarkable cation-exchange capacity, CEC, enables them to be used as an additive to fertilizers so as to increase the nutrient retention capacity of the soil thereby increasing the fertility of the land and boosting the crop yield. Being an agrarian nation, the Indian economy would be greatly affected by enhanced fertility of the land following a cost-effective manner of nutrient addition and retention, wherein fly ash based zeolites would play a very significant and crucial role. This is also due to the inherent nature of the zeolites, which makes them an excellent 'sorbent' (i.e., a material with good sorption characteristics), which helps cleaning up of the polluted soils and water bodies. Also, the sorption characteristics of zeolites can also be employed for removal of ammonia from the waste water.

Moreover, the physical, chemical, mineralogical, bacteriological and thermal characterization of the synthesized zeolites has been carried out for determining their suitability in various industrial and environmental applications. Incidentally, studies conducted by previous researchers for synthesizing fly ash zeolites, for their usage in agri- and aqua-culture, and other environmental clean-up projects, have been generally restricted to laboratory, which often turn out to be uneconomical and tedious. This calls for development of appropriate process(es) apt for large-scale industrial production of the ash based zeolites, exhibiting high CEC value, for their utilization in various walks of the society (viz., environmental clean-up activities such as contaminated soil remediation, sludge sediment treatment, heavy metal removal from water and clean-up of large water bodies). It is believed that opportunely synthesized zeolites could become a panacea for sustainable development.

Structure of zeolites

Zeolites are crystalline, hydrated aluminosilicates of tectosilicate type (Mumpton, 1985) i.e., a three-dimensional framework of SiO_4 tetrahedral having their four oxygen atoms shared by the adjacent tetrahedra. Some of these quadrivalent Si atoms are replaced by the trivalent Al atoms thus creating a deficiency of a positive charge which is responsible for its cation exchange capacity (CEC). This charge is balanced by monovalent ions such as Na^+ and K^+ or divalent ions such as Mg^{2+} and Ca^{2+} elsewhere in the structure. The deficient oxygen atoms in zeolites have more affinity for divalent cations than for monovalent cations. These charge balancing cations are exchangeable with other ions (viz., NH_4^+, Cs^+, Sr^{2+}) depending on the sizes of the pores and ions (Querol *et al*., 2002).

The general formula for a zeolite is $M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$ 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 Al_2O_3 and SiO_2 are the structural cations because they form the tetrahedral framework with oxygen (Mumpton, 1985).

Types of zeolites

Based on their genesis, zeolites are of two types, viz. natural and synthetic.

Natural zeolites

Natural zeolites are formed due to geological and environmental effects. The ash from volcanoes settles in closed environments, such as lakes, and undergoes chemical changes in the presence of an alkaline medium resulting in the formation of zeolites. Some common natural zeolites. Clinoptilolite is the most common natural zeolite having a Si/Al ratio of 5.7 (Zabochnicka-Świątek, 2010) and is widely used in fertilizers because of its strong affinity for ammonia. It has also been used for removing caesium and strontium from radioactive wastes. Clinoptilolite also acts as a substrate for the growth of microorganisms, especially the nitrogen-fixing bacteria, azotobacter (Andronikashvili *et al*., 2008)

Synthetic zeolites

Synthetic zeolites are created artificially from materials capable of contributing a silica-alumina gel such as fly ash, kaolin, river sediments, etc (Wu *et al*., 2008; Reyes, 2011; Holmes *et al*., 2012; Georgiev *et al*., 2013). Apparently, such zeolites will contain impurities which were originally present in the parent raw material.

Methods of synthesis of zeolites

Different methods of synthesizing zeolites from fly ash have been devised depending on the reactants and their reaction conditions.

Hydrothermal method

In hydrothermal method, the fly ash is treated with an alkali solution and further cooled down for crystallization. The reaction may be carried out in open or closed environment. This is the simplest and most popular method for obtaining zeolites (Adamczyk, 2005; Derkowski *et al*., 2006; Fansuri *et al*., 2008; Jha, 2013; Jha *et al*., 2011; Cundy, 2005). Further, (18) used the rudimentary hydrothermal method to synthesize zeolites from Class F fly ash at atmospheric pressure (refer Table 3.1). The thermostability of zeolite structures obtained (viz. Na–X, NaP1 and sodalite) was analysed at 300°C, 500°C and 700°C. The water absorption efficiency of Materials X and P were measured to be equally good as silica gel. High ion selectivity for heavy metals have also been observed for all the zeolites based on their atomic weights (viz. $Cd^{2+} > Cu^{2+} \approx Zn^{2+} > Co^{2+}$). Material X has been seen to contain a high amount of Na-X which has a possibility to replace the commercial 13X. It can also be used as a gas absorbent due to the wide micropores and high thermostability. The authors have claimed the method to be economical and energy efficient although non-zeolitic impurities were also produced.

Fusion and hydrothermal method

The alkali is fused with fly ash at temperatures ranging from 30°C to 750°C. This enables the crystalline phases in the raw material to dissolute to an amorphous state and, subsequently, hydrothermal treatment is carried out, resulting in higher yield of zeolites compared to the conventional hydrothermal method (Ojha *et al*., 2004; Terzano *et al*., 2005; Wu *et al*., 2008; Jha, 2013). Further, (Ojha *et al*., 2004) have synthesized X-type zeolite by alkali fusion followed by hydrothermal treatment at 90°C.

The raw fly ash was initially sieved, calcined (to remove unburnt carbon) and treated with HCl (to remove iron and hence increase the activity for zeolitization). They have reported maximum values SiO_2/Al_2O_3 ratio and degree of crystallinity at a fusion temperature of 550°C. Also, the maximum SiO_2/Al_2O_3 ratio = 1.72 has been achieved at an aging time (stirring time at room temperature) of 18 hours. The authors have found that 6 hours of hydrothermal treatment was the optimum time duration for maximum surface area of zeolites. (Wu *et al*., 2008) have used river sediments collected from Suzhou Creek, Shangai, China to synthesize zeolites since they contain silica (69.0%) and alumina (11.8%). The sediment was initially heated at 800°C for 30 minutes resulting in the transformation of illite and kaolinite into amorphous state. Further, the sample was fused with NaOH at different Si/Al ratios by adding aluminium hydroxide hydrate followed by heating at 350-750°C for 15min - 4hours. Liquid/solid ratio was kept at 2.5-20ml/g by adding distilled water and the solution was stirred at 95°C for 2-24 hours. Na-P1, Na-X, hydroxysodalite, F Linde A and Faujasite were obtained at different proportions depending upon the synthesis parameters as shown in Tables 3.2 and 3.3. The authors have also verified previous findings (33) that reactants having low Si/Al ratio results in the synthesis of zeolites having low Si/Al ratio while a high Si/Al ratio of reactants produces zeolites with high Si/Al ratio. A crystallization time of 2 hours is sufficient for zeolitization since no effect has been noticed beyond this temperature. Researches have been conducted for the application of natural and synthetic zeolites in agriculture. High plant growth and better yield are the common observations of many such studies.

Molten salt method

In molten salt method, a mixture of fly ash, a base (viz., NaOH, KOH or NH_4F) and a salt (viz., KNO_3, $NaNO_3$ or NH_4NO_3) is heated to molten temperatures. The absence of water is the main advantage of this method (Park *et al*., 2000; Choi *et al*., 2001).

Ultrasonic method

The fly ash or other aluminosilicates, such as kaolinite, along with a mineralizer (viz. alkali) is subjected to ultrasonication. This allows a larger amount of fly ash particles to dissociate into the suspension resulting in a higher yield of zeolites. Moreover, this process results in the evolution of heat, even up to 75°C, within a short time (viz., 10 minutes) thus avoiding an additional hydrothermal treatment of the mixture (Andaç *et al*., 2005; Kim *et al*., 2010; Hollman *et al*., 1999; Akari *et al*., 2013).

Microwave assisted hydrothermal method

Microwave assisted hydrothermal method is a technique to accelerate the ordinary hydrothermal process by initially microwave heating the raw materials and further subjecting the mixture to hydrothermal treatment

Factors affecting the synthesis

The factors affecting the synthesis of zeolites are Si/Al molar ratio of reactants and products, initial material composition,

Table 4.1 Synthesis proportion and zeolites obtained (Derkowski *et al.*, 2016)

Material	Fly Ash (g)	NaOH	NaCl	Temp (°C)	Reaction time (hr)	Zeolites synthesized	Si Al	Na+K+Ca+Mg Si
X	10	200ml-3M	NIL	75	24	Na–X	1.10	0.59
P	10	200ml-1M	100ml-3M	105	24	NaP1	1.43	0.45
S	10	400ml-5M	200ml-3M	105	24	Sodalite	1.21	1.06

Table 4.2. Details of zeolites synthesized from river sediments [60]

Zeolite obtained	Si/Al of sediment	NaOH/sediment (g/g)	CEC (cmol/kg)	SSA (m^2/g)	Si/Al of zeolite
Na-P1	5	1.6	295	40	1.67
Hydroxysodalite	1	2	115.6	16.5	0.84

Table 4.3. Influence of Si/Al ratio of sediment on zeolites synthesized (Wu, 2016)

Si/Al of sediment	NaOH/sediment (g/g)	Zeolite(s) synthesized
5	1.2	Na-P1
	2	Na-P1, Na-X, Hydroxysodalite
1-3	1.2	Faujasite, Hydroxysodalite, and F Linde A

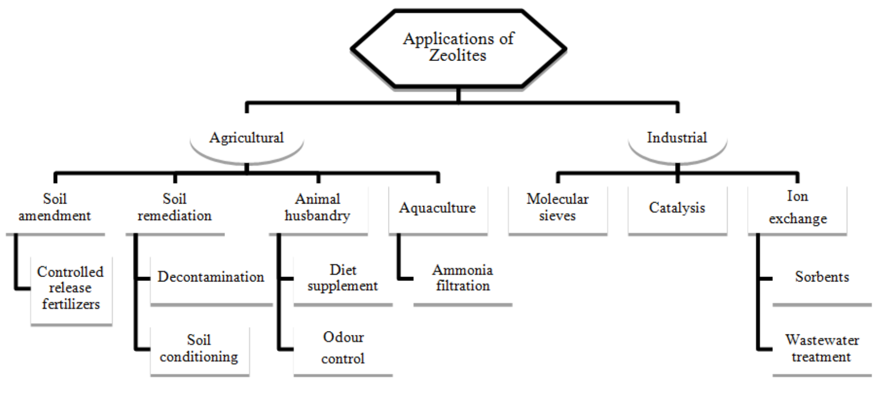

Fig. 1.1 Different agricultural and industrial applications of zeolites

pH, reaction time, temperature and pressure (Barth-Wirsching, 1989). The zeolitization process can be augmented by lowering the silica content in fly ash using a suitable silica reduction technology thereby increasing the concentration of alumina. Also, the physical, chemical and mineralogical properties of the synthesized products decide their applications in agriculture and industry.

Applications of zeolites

Zeolites possess excellent properties such as ion exchange capacity, dehydration and rehydration abilities and adsorption. They are molecular sieves which can selectively absorb ions that fit into the niches in their structures (Ahmaruzzaman, 2010) Fig. 1.1 shows a brief outline of the various agricultural and industrial applications of zeolites

Agricultural applications

The high cation exchange capacity (CEC) and water retention of zeolites make them useful for agricultural purposes (Mumpton, 1985). Traditionally, zeolites have been used in agriculture in Eastern Europe, Japan and Cuba (http://www.lenntech.pl/zeolites-applications.htm accessed on 8th July, 2013) (Burriesci *et al*., 1984) have carried out tests on zeolites synthesized from Lipari pumice by adding them to the soil both directly and as fertilizer mixtures for spinach cultivation. The authors have recommended the application of less than 50g/m^2 of Faujasite, due to its high water adsorption capacity, to the soil before sowing and the addition of fertilizers after the germination phase. (Burriesci, 1984) have synthesized zeolites (viz. faujasite and hydroxy-sodalite) from Lipari pumice by hydrothermal treatment with aqueous NaCl having 12% wt of NaOH for 7h at 95°C. They have reported a significant increase in yield and fruit sizes on application of these zeolites on Vitis vinifera and Prunus persica in Italy with their yield having doubled on application of NPK fertilizer with 90% zeolites and 25% respectively.

(Kikuchi, 1999) has used fly ash for the synthesis of zeolites and potassium silicate fertilizer and for flue gas desulfurization. (Polat *et al*., 2004) have studied the use of clinoptilolite in agriculture for fertilizer efficiency, gas and water absorption, ion exchange and soil amendment. Zeolites retain the fertilizers without breaking down and release them when required by the plants thus preventing the leaching of these fertilizers from the root zone. The application of zeolites has been observed to have enhanced the yield of apple, vegetables, grapes and other fruits. They absorb gases in animal husbandry sheds which reduces the undesirable odours due to ammonia and H_2S content. In fish tanks, they have been used to remove the high concentration of ammonia in the water. They also remove Pb, Cd and Cu present in contaminated soils. Clinoptilolite absorbs toxins in animals thus performing the role of a mycotoxin binder (Elliot, 2005) have investigated the properties of zeolite as controlled release fertilizers. They have demonstrated that by adjusting the reaction time, different types of zeolites can be synthesized. They have also listed the existing diversified zeolite markets which include agricultural, industrial, commercial and household uses (Terzano *et al*., 2005) have synthesized zeolites in agricultural soil under alkaline condition by addition of either fused fly ash or NaOH powder at 30°C and 60°C for six months. They have reported the almost complete conversion of the fly ash into zeolite X and zeolite P. Their results have validated existing studies showing that low Si/Al ratio at high temperatures (i.e. 60°C) favours formation of zeolite P while high Si/Al ratio at low temperatures (i.e. 30°C) results in the synthesis of zeolite X. The authors have stated that the addition of fly ash stimulated the Si and Al in soil to take part in the zeolitization by partial dissolution due to the alkaline medium which was inferred from the fact that the amount of zeolites synthesized was higher than the quantity of fly ash added. The pre-treated fly ash also biased the reaction towards the synthesis of a certain zeolite, viz. zeolite X which is preferred because of its higher cation exchange capacity due to lower Si/Al and higher specific surface area compared to zeolite P (Chang, 1998) The organic matter and minerals present in the soil did not hamper the synthesis (Fansuri *et al*., 2008) have synthesized Na and K zeolites from fly ash at 140°C and 150°C for 24 hours with and without agitation by varying H_2O/Al ratios from 25 to 420. Analcime was the main zeolite synthesized at the optimum H_2O/Al ratio of 57.4. These zeolites were applied up to 5 wt% to yellow gravelly loamy sand and Bassendan sand for pot plant trials of canola, spinach and wheat. The authors have observed the amounts of Cd and Hg in plant shoots to decrease with increase in zeolite (Andronikashvili *et al*., 2010) have investigated the effects of natural zeolites viz. analcime and phillipsite on grape cultivation by conducting five trials, the first being the control soil without any mineral fertilizer. The zeolites were added individually and also by mixing with equal amount (by weight) of manure. They reported that the use of analcime increased the yield, after two years, by 115% when added alone and 160% when mixed with manure while the same methodology using phillipsite, after one year, were 83% and 146% respectively. The zeolites increased the cation exchange capacity of the soil and also created a favourable site for growth of nitrogen-fixing microorganisms. The authors have also reported an increase in the sugar content by 5-27% and a decrease in acidity from pH =3.75 to 4.52.

The following are the sub sets of agricultural applications.

Controlled release fertilizers (CRFs)

Fresh swine or chicken manure can be used to saturate zeolite with ammonia. This ammonia-saturated zeolite, when applied to the soil, acts as a slow release nitrogen fertilizer (Parham, 1989; Eberl, 1993) Sodium, in high concentration, is toxic to plant life (Blumwald *et al*., 2000; Kronzucker, 2011) and hence sodium based zeolites are not recommended for agriculture (Blumwald *et al*., 2000).

Soil conditioning

Zeolites can help to increase the porosity of the soil. They also favour the growth of microorganisms such as azotobacter (Andronikashvili *et al*., 2008).

Aquaculture

In fish hatcheries, ammonia is formed by the decomposition of excrement and unused food due to the closed environmental conditions preventing proper recirculation or purification which is the main cause of disease and mortality in fish. Zeolites can be added to the fish tanks and shrimp ponds as a sorbent for removal of ammonia, hydrogen sulphide and carbon dioxide (Moriyama *et al*., 2005; Mumpton, 1985; Nguyen, 1998)

Animal husbandry

Many researches have been conducted on the effects in addition of zeolites to feeds of swine (Kondo, 1968; Han, 1975; Derkowski *et al*., 2006; Hayhurst *et al*., 1980) and (Nguyen, 1998) has reported an improvement in the calorific efficiency of the poultry due to the zeolite intake (Mumpton, 1982). Zeolites have even been found to be effective in preventing certain metabolic diseases in cows (Papaioannou *et al*., 2005).

Water treatment

Zeolites have been used for sludge and water purification by the removal of heavy elements such as SO_x and CO_x (Czurda, 2002) and heavy metals such as Ni (Harja, 2012) They have also been used for the removal of ammonia from wastewater (Nguyen, 1998; Querol *et al*., 2002; Fan, 2008; Reyes *et al*., 2011).

Industrial applications

Gas separation and removal: Researchers (Querol *et al*., 2002; Nascimento *et al*., 2012) have used zeolites for the separation and removal of gases such as CO2, SO2 and H2O from low grade natural gas streams. Zeolites have been employed on On-Board Oxygen Generating Systems (OBOGS) for removing nitrogen from the compressed air for supplying oxygen to cabin crews in aircrafts at high altitudes (Holmes, 2012). The following are the applications of zeolites in industrial purpose.

Petrochemical industry

Zeolites have been used for multifunctional purification of mineral oils (Speight, 1991) and for adsorptive purification in reconditioning and regeneration of used lubricating oils (Betton, 1997). They also act as catalysts in petroleum refining (Belviso *et al*., 2011; Newsam, 1986) (Zabochnicka-Świątek, 2010) have used clinoptilolite, a natural zeolite, to remove ammonia from water. In water, ammoniacal nitrogen ($N\text{-}NH_4^+$) is present in two forms, viz. ammonia (NH_3) and ammonium ion (NH_4^+). They have studied the effects of zeolite concentration and exposure time on the $N\text{-}NH_4^+$ removal and have calculated the degree of ammonia removal and the sorption capacity. The effect in the exposure time has been observed to be insignificant in the amount of ammonia uptake.

Molecular sieves

Zeolites have been used to separate molecules based on their sizes and shapes. They have also been utilized for trapping molecules for analysis (Chang *et al*., 1999; Zhang *et al*., 2012).

Oil spill clean-up

Zeolites synthesized from fly ash have been successfully employed to clean-up oil spills in water. Zeolite-X acts as an excellent hydrophobic sorbent of the oil present in water (Sakthivel *et al*., 2013; Klamrassamee *et al*., 2010) have synthesized zeolite from fly ash by fusion and hydrothermal method. They have checked its ability to remove water in ethanol solution and have reported a water adsorption of 95% from the ethanol. (Otal *et al*., 2005) have analysed the efficacy of fly ash zeolites and commercial zeolites for purification of MSW landfill leachates and liquid cattle farm waste by stirred tank test and column test. In the stirred tank, the increase in the sedimentation time and agitation time have not shown any increase in the purification of the sample. The results of the column test have shown better reduction of chemical oxygen demand (COD), total kjeldahl nitrogen (TKN) and $P\text{-}PO_4$ at a lower flow rate (viz., 50ml/min). (45) have studied the adsorption of heavy metals (viz. Zn, Cu, Mn and Pb) using zeolites synthesized from fly ash by hydrothermal method. The concentrations of metals varied from 100 to 3000 mg/l. The authors have concluded that the adsorption capacity of the fly ash increased 2 to 25 times due to zeolitization.

Building materials and construction

Natural zeolites have been used as admixture to prevent bleeding, segregation and delamination of concrete for stabilization of cement volume (Feng, 2005).

MATERIALS USED FOR SYNTHESIS OF ZEOLITES

Fly ash

Being an industrial by product, fly ash is inexpensive and found in abundance. It contains a large amount of silica and alumina along with other impurities.

Sediments

River sediments have been successfully employed to synthesize zeolites using fusion and hydrothermal method (Wu *et al*., 2008).

Kaolinite

Kaolinite when heated to high temperatures, such as 550°C, forms metakaolinite

Conclusion

Following are the main conclusion drawn from the present study.

- Fly ash is a by product generated in an thermal power plant, which is considered as a waste material and which can be utilized to manufacture useful product called as Zeolite
- Zeolite is a porous material which has high CEC and which help to trap required material in its porous structure.
- Zeolites can be effectively used for cleaning up of water bodies, by spreading the zeolites on water surface and allowed to sorb the unwated constituents present in that perticular water body.
- Fly ash synthesised zeolites can be used for removal of heavy metals by hydrothermal method.
- Fly ash zeolites and commercial zeolites are used for purification of MSW landfill leachates and liquid cattle farm waste by stirred tank test and column test. In the stirred tank, the increase in the sedimentation time and agitation time have not shown any increase in the purification of the sample.

- zeolites synthesized from Lipari pumice by adding them to the soil both directly and as fertilizer mixtures for spinach cultivation, which increases water holding capacity of the soils.

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