

International Research Journal of Environment Sciences_ Vol. 4(3), 93-99, March (2015)

Review Paper Zeolite Synthesis Strategies from Coal Fly Ash: A Comprehensive Review of Literature

Khadse Shaila¹, Dawle Nisha¹, Patil Pralhad¹, Panhekar Deepa² ¹LIT, RTM Nagpur University, Nagpur, INDIA ²Department of Chemistry, Dr. Ambedkar College, Deeksha Bhoomi, Nagpur, INDIA

Available online at: www.isca.in, www.isca.me Received 6th January 2014, revised 25th February 2015, accepted 13th March 2015

Abstract

The ever increasing energy demand in developing world will result in sustainable increase in the fly ash generation, which will remain a cause of concern as far as its management is concerned. However, technological advance may prove to be effective in fly ash management as well as its possible utilization through the zeolites. The zeolites are known to possess many beneficial properties (such as ion-exchange property), however, its cost effective production using fly ash as a raw material has still not been standardized. In view of this, the present study (literature review) was carried out to understand the evolution of zeolite synthesis strategies adopted by different researchers. The literature clearly indicates that zeolite synthesis depends on physico-chemical properties of the raw material as well as reaction mixture. However, it also suggests that the current state of knowledge can be readily used for further advancement of the zeolite synthesis processes on commercial level using fly ash as the primary source of raw material.

Keywords: Fly ash, management, zeolites, synthesis strategies, ion-exchange.

Introduction

The rapidly growing energy demand in developing world in general and India in particular demands that high energy generation should be achieved. Though there are different ways to generate energy; historically, coal-based power generation has been predominant in India. Thermal power plant plays an important role in fulfilling the growing energy demand of the people¹. Currently, coal-based thermal power installations in India contribute about 65% of the total installed capacity for electricity generation. Indian coals have very high ash content (25 and 45%) and typically, the coal with an ash content of 40% is widely used in the power plants of India. As a consequence, a huge amount of fly ash is generated in thermal power plants, causing several disposal-related problems. As far as the disposal of fly ash is concerned, presently, the fly ash utilization for different purposes is less than 10% (of that is produced) in India, which is significantly less than that has been achieved in other countries. The major fly ash utilization area is the construction industry, which utilizes approximately 50% of the generated fly ash (due to its proven availability) for several applications as admixture in cement/concrete, lime pozzolanic mixture (bricks/blocks etc.). The other usage of fly ash are Low lying area fill (17%), Roads and Embankments (15%), Dyke Raising (4%), Brick manufacturing (2%) and zeolite etc.

Zeolites are important in view of their industrial applications, such as in ion exchange, as molecular sieves, catalysts, and adsorbents. Fly ash has the potential to be converted into zeolites. There are three important uses for zeolites in industry, the most important being catalysis, as Zeolites are extremely useful as catalysts for several important reactions such as cracking, isomerisation and hydrocarbon synthesis. Since, the reactions can take place within the pores of the zeolite, it allows a greater degree of product control and the others include gas separation (the porous structure of zeolites can be used to "sieve" molecules having certain dimensions and allow them to enter the pores) and ion exchange (applications in water softening devices, in detergents and soaps, also it is possible to remove radioactive ions from contaminated water).

In the backdrop of above information, it is apparent that the fly ash, if managed and utilized properly can be a beneficial item for possible use in different areas. However, the current practice of utilizing the fly ash is restricted in specific domains, such as construction sector, as a filler, etc. Hence, an attempt has been made in this study to review the literature for identifying the research gaps as far as zeolite synthesis is concerned.

Methodology

In this study, past literature has been reviewed to identify the evolution and progress of the fly ash management strategies and applications with a special emphasis on its ion-exchange property. The research gaps, which exist in this domain, have been identified on the basis of the literature review. The contents of the research articles were reviewed using the principles of content analysis and care was taken to ensure the originality of the views by using the original terminology. Furthermore, the literature was reviewed (as a discursive prose) to synthesize and evaluate it according to the guiding concept for identifying most important future research questions. In addition to this, utmost importance was given to use the literature published in standard scientific journals.

Results and Discussion

Currently, the applications of synthetic zeolites in different areas have noticeable presence over their counterpart i.e. natural zeolites. This is primarily due to the nature of synthetic zeolites, which are the purity of crystalline products and the uniformity of particle sizes. The customized zeolite synthesis offers many advantages over the natural zeolites, which include the ability to engineer (with wide variety of chemical properties, pore size and thermal stability) the zeolites for specific application. Besides, the natural zeolites have certain drawback like they do not show appropriate ion affinity, for example toward Cu, Cs and Co and Ur ions. Thus, the need for synthesizing more stable, efficient and predictable zeolites is omnipresent and may be ever increasing due to their possible applications. Conventional zeolite synthesis involves the hydrothermal crystallization of aluminosilicate gels, or solutions in a basic environment. The nature of zeolite affects when the crystallization takes place in a closed hydrothermal system that is undergoing increasing temperature. The autogenous pressure and varying time, composition of the reaction mixture (silica to alumina ratio; OH⁻; inorganic cations), reactants and their pretreatments, temperature of the process, reaction time, pH, etc. affect the nature of zeolite synthesized. In addition to this, the increasing demands of zeolite (qualitative and quantitative) warrants that the zeolite synthesis be carried out in a continuous or batch process. Thus, it is apparent that the process of synthetic zeolite synthesis is dynamic in nature and offers numerous challenges for its standardization. Hence, a periodic literature review is very essential for updating the knowledge regarding the effect of various experimental conditions, which govern the quality and quantity of synthesized zeolite.

Zeolite Synthesis Up to 2000: Zeolite A and faujasite (using specific conditions of temperature and chemical composition) was successfully synthesized and then compared its ion exchange properties for Cs⁺ ions which shows 19% for zeolite A and 39% for faujasite which is applicable for waste-water treatment and radioactive waste immobilization³. During hydrothermal treatment, Si and Al contained in fly ash dissolve into basic solution which gives ring like structure and then gets converted into zeolite. Furthermore, authors have mentioned that seeding can selectively induce the formation of zeolite Y and eliminate the processes of induction and nucleation⁶. А conventional and microwave-assisted hydrothermal alkaline activation experiment was used to synthesize from fly ash. Authors reported that the zeolite synthesis is a function of temperature, time, and concentration of activation solution. Besides, zeolite types and its yields were also reported to be very similar when it was obtained from the microwave and conventional experiments, however, the activation time

was drastically reduced (from 24-48 h to 30 min) when a microwave was used⁷.

Zeolite Synthesis After 2000: Reactivity of fly ash towards zeolite formation is directly dependent on the SiO_2/Al_2O_3 ratio, Fe_2O_3 and CaO content. Authors reported that the subbituminous coal based fly ash with SiO_2/Al_2O_3 ratio of 3.47 is a suitable substrate for Zeolite-A synthesis⁸. Three types of zeolite (NaP1 zeolite, analcime and chabazite) were hydrothermally synthesized with the fusion of fly ash and NaOH solution. The maximum conversion rate from fly ash to single zeolite was about 4075, and the total conversion rate 6080. Authors stated that the factors which influence variety and its conversion rate into zeolite were vortex, viscosity, temperature, reaction time, and NaOH concentration⁹.

Zeolite structures can be identified by considering a neutral SiO₂ framework and then substituting AlO₂⁻⁻ for SiO₂. The resulting structure shows a net negative charge, which is balanced by cations (for instance, Na⁺, K⁺, or NH₄⁺) and many of these cations are mobile and free for exchange. This ion-exchange property accounts for the greatest volume use of zeolites today¹⁰. Coal fly ash was activated by hydrothermal treatment with different concentrations of NaOH solutions to synthesize the zeolites, Na-P1 and hydroxysodalite. Authors further stated that, such modification enhances fly ash significantly with respect to specific surface area and cation exchange capacity. Specific surface area increased from 1.0 m²·g⁻¹ to a maximum of 62.7 m²·g⁻¹ while cation exchange capacity rose from 25 mmol/100 g to a maximum of 300 mmol/100 g¹¹.

Alkali fusion followed by hydrothermal treatment was used for the synthesis of X-type zeolite from coal fly ash. Beside, the cost was observed to be almost one-fifth of that of commercial 13X zeolite available in the market. It was widely reported that the crystallinity was a function of fusion temperature¹². Zeolite structure development and exchange capacity is a function of variations in pretreatment steps and sodium aluminate addition. They further stated that infrared is a better option for estimating crystallinity of the zeolite during hydrothermal treatment of fly ash by using step-change of temperature in synthesis¹³. The zeolite synthesised was a pure form, single phase and high crystalline. Authors stated that during hydrothermal treatment step-change of synthesis temperature plays an important role in reducing the overall synthesis time while maintaining a high degree of crystallinity for the samples¹⁴.

Zeolite was prepared from coal fly ash using the fusion method and specified that a ratio of 2.25 between coal fly ash and NaOH was responsible for maximum cation exchange capacity (of 219.7 meq/100g at 2 hour fusion time)¹⁵. Furthermore adsorption and desorption properties of the ion exchange resins is dependent on many factors, however, the feed concentration is probably the strongest of them (factors) all¹⁶. Zeolite Na-P1 was synthesized from fly ash for by using optimized synthesis conditions (NaOH/SiO₂ molar ratio was 0.59 at an aging temperature of 47°C for 48 hours the purpose of elimination of trace elements from brine. The reverse osmosis was reported to be effective in removing a large percentage of B, V, As, Mn, Ni, Pb, Fe, Zn, Mo, Sr, Ba, Mg, Cd and Se from a brine concentrate by using zeolite Na-P1¹⁷.

On the basis of estimated values of thermodynamic parameters such as heat of adsorption and standard Gibbs free energy that the adsorption of Cr (VI) on zeolite NaX was found to be exothermic in nature¹⁸. X-type zeolite was synthesized by alkali fusion followed by hydrothermal treatment from the coal fly ash, which as per the authors is almost one-fifth of that of commercial 13X zeolite available in the market¹⁹. Addition of sodic or potassic reagent in the starting mixture reduces the stability field for zeolite N formation. Zeolite N can also be formed using zeolite 4. Al is used as a source of Al and Si though for longer reaction times at a specific temperature when compared with kaolin as the source material²⁰. Thus the coal quality plays an important role in the zeolification process, which directly affects the properties of zeolites, such as cation exchange capacity (CEC), specific surface area, specific gravity and particle size distribution²¹.

Authors clarified the mechanism of zeolite synthesis from fly ash by using various alkali solutions during hydrothermal reaction. During hydrothermal reaction, various physical and chemical properties investigated were crystal structure, surface structure and cation exchange capacity, of the obtained zeolites and the dissolved amount of Si^{+4} and Al^{+3} in alkali solution. The mechanism of zeolite crystallisation and the role of alkali solution play an important role on the synthesis reaction. The study showed that the OH⁻⁻ in alkali solution remarkably contributes to the dissolution step of Si^{+4} and Al^{+3} in coal fly ash, while Na⁺ in alkali solution makes a contribution to the crystallization step of zeolite P²².

Zeolite-A (FAZ-A) was patented nationally and internationally by using fly ash. Zeolite was used for the removal of lead. Authors studied rate constants using Lagergren's model indicating the reaction to be of first order. On the basis of available data, they concluded that the zeolite showed maximum capacity of 714.28 mg/g for lead²³. The fly ash conversion into zeolite was obtained by using [SiO₂]/ [Al₂O₃] ratio 1.4 to 2.5. In this the Si and Al contents of fly ash filtrates were used as starting material for alkaline hydrothermal conversion. The steps involved in zeolite synthesis were an alkaline fusion of the co-disposal filtrates, aging, and hydrothermal conversion by crystallisation at 100 °C. Different variables such as use of deionised water, different compositions of FA related staring material and different FA: NaOH ratios in fusion were investigated to increase zeolite formation²⁴. A geopolymer material was synthesized from Class F fly ash, by studying elevated temperature curing on phase composition, microstructure and strength development. It was observed that long procuring at room temperature before application of heat was beneficial for strength development in all studied material 25 .

Hence a new methodology was reported for the conversion of

fly ash into zeolite. Suitable operation parameters of the process were reported using a test unit, and the optimal conditions were found to be 2.5-3.5 mol/dm3 of NaOH and 0.88-1.10 dm³/kg of liquid/solid, sodium hydroxide charge from 2.2 to 3.9 mol/kg-CFA. The authors further stated that the zeolites obtained from a pilot plant had a higher cation exchangeable capacity than those from the test unit and were comparable to zeolites prepared using a conventional method²⁶. Fly ash based zeolite-A (FAZ-A) was synthesized for the determination of its optical brightness. The improvement of optical brightness was done by using pretreatment of fly ash, acid treatment, lime treatment which in turn controls the colour development of zeolite sample & used as detergent builder²⁷.

Fly ash was converted into single phase zeolite from fly ash by dialysis. NaOH-NaAlO2 solution was used to maintain SiO2/Al2O3 molar ratio of the solutions from 0.9 to 4.3. The Na-X zeolite was produced at SiO₂/Al₂O₃≥1.7²⁸. Zeolites from two different fly ashes were obtained from different Lignite Power Plants and the products were tested for their potential of retaining heavy metals from a contaminated soil. It was observed that for lower FA/NaOH ratios, the excess of NaOH seemed to be prohibitive for zeolite growth, while for the higher ratios, the NaOH quantity seemed to be insufficient for the effective activation of the fly ashes²⁹. During conversion of fly ash to zeolite fractionation of immobilized phosphorus indicated that Fe + Al-P increased most significantly and consistently among all the phosphorus fractions. Increase in dissociated Fe₂O₃ and specific surface area probably accounted for the enhancement in phosphate immobilisation capacity of synthesized zeolites compared to the corresponding fly ash³⁰

Zeolite was obtained by refluxing of fly ash in NaOH solution by refluxing under microwave irradiation for 1 h. During pretreatment, the amorphous aluminosilicate of fly ash was dissolved and its dissolution rate was found to be much faster than that of conventional air oven. Author also reported that the cationexchange capacity (CEC) of a single-phase Na-A zeolite formed at $SiO_2/Al_2O_3 = 0.8$ was 508 cmol/kg which is close to the 550 cmol/kg of the commercial Na-A zeolite³¹. Pure form zeolite A was synthesized using four concentrations of NaOH solution to dissolve Si source from fly ash and with the addition of Al source, to prepare initial gel Author synthesized pure zeolite A by using NaOH concentrations, 1.67, 5 and 6.67 M; the synthesis temperature, 100 °C and 340, 250 and 190 min.as a crystallisation time. Furthermore they reported that the higher NaOH concentration was used, the shorter crystallisation time of zeolite A was required and the distribution of particle size zeolite A was achieved to be narrower³².

During the zeolite synthesis process the changes of mineralogical-chemical composition, cation exchange capacity (CEC), and phosphate immobilization capacity (PIC) was investigated. The zeolites were obtained by using the parameters such as temperature (40-120 0 C), liquid/solid ratio (1-18 ml/g), NaOH concentration (0.5-4 mol/L) and reaction time (2-72 h). Authors reported that lower the ratio of K₂O,

MgO and Fe₂O₃, TiO₂ content were related to the solubility of the oxides while the increase in Na₂O and CaO was due to the increase in cation exchange capacity³³. Na-A,-X and -Y zeolite was prepared by using high silicon fly ash by alkali fusion followed by hydrothermal treatment at 100 °C for 12 h. Different types of zeolite having different degrees of purity were synthesized by changing Si/Al ratio of the reaction mixture from 1.6 to 3.0. The characterization studies showed that the zeolite was crystalline, had a very high cation-exchange capability of 4.9 mequiv. g⁻¹ and possessed relatively high specific surface area of about 434 m² g^{-1 34}.

An Italian coal fly ash was converted into zeolite with temperature of crystallisation ranging from 35 upto 90° C. It was reported that the zeolite X and zeolite ZK-5 were prepared by using both distilled and seawater. The formation of sodalite was competitive with zeolite X which shows a metastable behaviour at higher temperatures. Author concluded that the formation of specific zeolites required lower temperature when seawater was used³⁵. The transformation of mechanism of a fly ash into NaX zeolite was studied. Two synthesis systems were investigated at 30-50° C in absence or presence of external soluble silica. Authors described the zeolitisation mechanism in three steps such as dissolution of fly ash, dissolution of silica from fly ash and conversion fly ash into NaX. The various effects of silica were discussed in relation with the zeolitisation mechanisms³⁶. Later on again conversion of a French coal fly ash into NaX zeolite (faujasite) by using the optimal composition (1SiO2:0.36Al2O3:3.8NaOH:72.7H2O) for the synthesis. It was observed that the addition of soluble silica leads to a better solubilisation of the FA, about 20% more Al being mobilised. Author stated that the zeolitisation reaction was delayed when silica was added, the maximum faujasite content being reached after about 50 days instead of about 20 days³⁷. The direct route of zeolite synthesis was preferred by using soft reaction conditions that resulted in a high yield of low cost zeolite with large crystal agglomerates. For both zeolitisation routes, the nature of alkali (KOH, NaOH, and LiOH), the alkali/MFA ratio (0.23-1.46), and crystallisation temperature and time (90-175 °C; 8-24 h) were evaluated. The study demonstrated that aluminum modified W zeolite shows applicability of removal of arsenic (99%) from Na2HAsO4 · 7H2O solution containing 740 ppb of As³⁸.

Zeolite Synthesis in Recent years: Synthetic basic sodalite, $Na_8[AISiO_4]_6(OH)_2 \cdot 2H_2O$, cubic, P43n was synthesized by alkaline activation of amorphous aluminosilicate glass obtained from fly ash. Geopolymerisation include treatment with high concentrations of a NaOH solution at 90 °C for 24 hours. The bulk modulus was determined using a diamond anvil cell up to a pressure of 4.5 GPa³⁹.

Chemical composition analysis of raw fly ash materials and zeolitic products from five different Brazilian fly ashes were conducted. Content of SiO₂ and Al₂O₃ was above 70 wt. % in all fly ashes. Hydroxy-sodalite zeolite was formed in all samples. NaP1 zeolite was formed in fly ashes with high content of Ca

while X zeolite was formed from the fly ashes with high content of Al. Cation exchange capacity values of the zeolitic materials were 40 times higher than fly ash samples, potential for use as ion exchangers⁴⁰. High phase purity of zeolite A was synthesized from coal fly ash. The formation of zeolite was monitored by using in situ ultrasonic system and was complemented by use of ex situ technique. It was observed that the comparable ultrasonic signals were generated when both clear and unseparated fly ash based precursor solutions were used during the zeolite synthesis process⁴¹.

The crystallisation mechanism of X- and A-type zeolites from fly ash was reported by analysing the role of Mg and Ca ions during treatment with artificial sea water. The crystallisation mechanism includes pretreatment by fusion with NaOH at 550°C by using artificial sea water at room temperature (25°C). The results indicated that Mg induces the formation of zeolite domains that act as templates for the crystallisation and growth of both X-type and A-type zeolites⁴². Zeolite was synthesized from fly ash and rice husk ash and studied the effect of amorphous silica content on crystallization time. Fly ash was mixed with amorphous silica in the ratios of 10:0, 8:2, 7:3, 6:4 and 5:5 (wt/wt). It was observed that the mixture of fly ash and amorphous silica in ratio of 7:3 generated the highest yield and crystallinity of zeolite (faujasite type). FTIR spectra exhibited the presence of internal Si-O-Si and Si-O-Al asymmetric stretching mode and morphology studies indicated an octahedral crystal of faujasite Author reported that the CEC and specific surface area of faujasite were 3.6 meq/g and 233 m²/g, respectively⁴³. A raw material containing blends of circulating fluidized bed combustion (CFBC) fly and bottom ashes was used for geopolymer synthesis. Authors reported that the effective alkali fusion was achieved at 350°C for 0.5 h. The results suggested that by a moderate alkali-fusion pretreatment at temperatures slightly higher than the melting point for sodium hydroxide (318 °C), low-reactive low reactive CFBC fly ash (CFA) can be recycled together with CFBC bottom ash (CBA) for production of value added geopolymer composites⁴⁴.

The rate of zeolite N synthesis was a function of temperature and type of clay minerals (such as kaolinites and montmorillonites) used. They further reported that Zeolite synthesis was more sensitive to water content and temperature when sodium was used in initial batch compositions⁴⁵. Fly ash and bottom ash (with high crystalline silica content) from the coal-fired boilers within the paper industries was used for synthetic zeolite production. Authors concluded that the type of zeolite synthesis method (direct conventional i.e. one-step synthesis or two-step i.e. sodium silicate preparation and consecutive zeolite A synthesis) used resulted in different amount of product⁴⁶. Na-zeolites were synthesized from Tunisian natural illite clay by alkaline fusion and conventional hydrothermal alkaline activation. In both cases, the synthetic zeolite products show better cationic exchange capacities compared with the raw material. However, the fusion method yielded a product with high crystallinity, good cation exchange properties and better surface area accompanied by shorter reaction times⁴⁷

SUZ-4 zeolite was prepared by hydrothermal technique under autogenous pressure with SiO₂:Al₂O₃ ratio of 21.22 using silicasol and tetraethlyammonium hydroxide as a silica source and a template, respectively. Authors concluded that highly crystalline SUZ-4 depended on enhanced temperature and time of crystallization conditions⁴⁸. Pure-silica-zeolite AST and LTA was manufactured by using the same structure-directing agent molecule at different concentrations. Authors argued that the deviations (structure-directing agent molecules can self-assemble into dimer or trimer complexes at different concentrations) from the Liebau's rules indicate that small changes in structure-directing agent chemistry, structure, and order in solution can have a great impact on the structure selectivity of the zeolite synthesis⁴⁹. Thermogravimetric method was applied for the control and determination of the quality of fly ash-derived zeolite in an industrial plant due to its short conversion factor 50 .

Two types of zeolites (Linde F and hydroxysodalite) were synthesized from fly ash by activation with NaOH and KOH. Blends of zeolites A and P was obtained at treatment with 3.1 m NaOH at 353 K. It was found that in both the types of zeolites, Na⁺ had been partially replaced by Ca²⁺. Zeolites crystallized preferably on particles having glassy surfaces and had quite a constant composition, unrelated to that of the surface⁵¹. The technological line of approach was automated to synthesize Na-P1 zeolite from the coal fly ash synthesized zeolite contained the properties as mesoporous (61%) and approximately six times higher the specific BET surface area than fly ash which proved it to be effective as an adsorbent for heavy metal pollutants⁵². The beneficial use of fly ash generated from thermal power plant was highlighted in development of bricks, cement manufacturing, ceramics, fertilizer, road construction, road embankment etc⁵³.

The applicability of fly ash as a zeolite was evaluated for the removal of lead from its aqueous solution. The adsorption was experimented by using variables metal ion concentration, contact time, pH, temperature and particle size. Adsorption isotherms, kinetics and also thermodynamic parameters have been evaluated and hence the process showed spontaneity, feasibility and endothermic in nature⁵⁴. A novel zeolite has been synthesized from fly ash. The applicability of synthesized zeolite have been studied for the adsorption of transition metal ions from paper industry waste water by using variable parameters such as pH, amount of zeolite, contact time. Adsorbent showed better adsorption for Ni²⁺ ion⁵⁵.

Very recently a low cost adsorbent fly ash was studied for the removal of phenol from aqueous solution. The adsorption study was experimented by using variable parameters. Authors reported that the uptakes of phenol by fly ash decreased by increasing particle size and pH but it increases with temperature. Fly ash showed better removal ability towards phenol and hence it can be used economically⁵⁶. Fly ash was modified was modified by alkali (FAN), dye (FAN-MO) and was used for the elimination of Ni²⁺ from its aqueous solution. The batch adsorption study was evaluated by studying pH, contact time, initial metal ion concentration and amount of adsorbent. Author reported the

influence of Cu^{2+} ions and Zn^{2+} ions on adsorption of Ni^{2+} ions on FAN and FAN-MO in binary and tertiary systems which showed gradual decrease of adsorption ability⁵⁷.

Conclusion

Millions of tons of waste materials are generated throughout the world, which pose serious threat to the sustainable development. The fly ash based zeolites provide an opportunity for effective as well as value added management of the fly ash. The literature review indicates that the zeolite processes developed include different methodologies, which primarily indicate modifications or alterations in pretreatment steps, alkali addition, etc. It gives formation of different structures that have potential for application in many fields (ion exchange capacity). The synthesis of zeolites from coal fly ash (which is abundant in India) with specific focus such as applications in water treatment could act as a more value-added high technology utilisation of fly ash.

Acknowledgement

Authors thank University Grants Commission, New Delhi, India for financial support.

References

- Bhattacharjee TC Kandpal, Potential of fly ash utilisation in India, *Journal of Cleaner Production*, 27(2), 151-166, (2002)
- 2. Doula M, Synthesis of a clinoptilolite-Fe system with high Cu sorption capacity, *Chemosphere*, **67**, 731-740, (2007)
- **3.** Foldesova M, Hudec P and Dillinger P, Chemically modified zeolites: Surfaces and interaction with Cs and Co, *Petroleum and Coal*, **49**, 60-63, (**2007**)
- 4. Hossein GM, Hossein K, Ali N.M, Ali M and Reza P.M, Ion Exchange Behavior of Zeolites A and P Synthesized Using Natural Clinoptilolite, *Iranian Journal of Chemistry and Chemical Engineering*, **27**, 111-117, **(2008)**
- 5. Wei-Heng S and Hsiao-Lan C, Conversion of fly ash into zeolites for ion-exchange applications, *Materials Letters*, **28**, 263-268, (**1996**)
- 6. Zhao XS, Lu GQ and Zhu HY, Effects of Ageing and Seeding on the Formation of Zeolite Y from Coal Fly Ash, *Journal of Porous Materials*, **4**, 245-251, (**1997**)
- Querol X, Alastuey A, López-Soler A and Plana F, A Fast Method for Recycling Fly Ash: Microwave-Assisted Zeolite Synthesis, *Environ. Sci. Technol.*, 31, 2527-2533, (1997)
- 8. Rayalu SS, Udhoji JS, Munshi KN and Hasan MZ, Highly crystalline zeolite - a from fly ash of bituminous and lignite coal combustion, *Journal of Hazardous Materials*, 88, 107-121 (2001)

- **9.** Wang Y, Guo Y, Yang Z, Cai H and Querol X, Synthesis of zeolites using fly ash and their application in removing heavy metals from waters, *Science in China*, **46**,967-976, (**2003**)
- **10.** Marcus BK and Cormier WE, Going Green with Zeolites, *Chemical Engineering Progress*, 1, (**1999**)
- 11. Woolard CD, Petrus K and Horst M, The use of a modified fly ash as an adsorbent for lead, *Water SA*, 26, 531–536 (2000)
- 12. Ojha K, Pradhan KC and Samanta AN, Zeolite from fly ash: synthesis and characterization, *Bull. Mater. Sci.*, 27, 555-564, (2004)
- **13.** Rayalu SS, Udhoji JS, Meshram SU, Naidu RR and Devotta S, Estimation of crystallinity in fly ash-based zeolite-A using XRD and IR spectroscopy, *Current Science*, **89**, 2147-2151 (**2005**)
- 14. Hui K.S and Chao CYH, Effects of step-change of synthesis temperature on synthesis of zeolite 4A from coal fly ash, *Microporous and Mesoporous Materials*, **88**, 145-151 (**2006**)
- **15.** Rungsuk D, Apiratikul R, Pavarajarn V and Pavasant P, Zeolite Synthesis from Fly Ash from Coal-fired Power Plant by Fusion Method, The 2nd Joint International Conference on "Sustainable Energy and Environment", E-042(P), Thailand, (**2006**)
- Silval DL, Brunner G, Desorption of heavy metals from ion exchange resin with water and carbon dioxide, *Brazilian Journal of Chemical Engineering*, 23, 213-218, (2006)
- 17. Musyoka NM, Petrik LF, Balfour G, Misheer N, Gitari W and Mabovu B, Removal of toxic elements from brine using Zeolite Na-P1 made from a South African coal fly ash, *International Mine Water Conference Proceedings*, 680-687, (2009)
- **18.** Pandey PK, Sharma SK and Sambi SS, Kinetics and equilibrium study of chromium adsorption on zeolite NaX, *Int. J. Environ. Sci. Tech.*, **7**, 395-404 (**2010**)
- **19.** Solanki P, Gupta V and Kulshrestha R, Synthesis of Zeolite from Fly Ash and Removal of Heavy Metal Ions from Newly Synthesized Zeolite, *E-Journal of Chemistry*, **7**, 1200-1205, **(2010)**
- Mackinnon IDR, Millar GJ and Wanda SW, Low temperature synthesis of zeolite N from kaolinites and montmorillonites, *Applied Clay Science*, 48, 622-630, (2010)
- **21.** Moutsatsoua A, Karakasia OK, Koukouzasb N, Itskosb GS and Vasilatosc C, Synthesis of zeolitic materials utilizing CFB-derived coal fly ash as a raw material, http://users.uoa.gr, accessed on 15Th March, (**2012**)
- 22. Murayama N, Yamamoto H and Shibata J, Mechanism of

zeolite synthesis from coal fly ash by alkali hydrothermal reaction, *International Journal of Mineral Processing*, **64(1)**, 1-17, **(2002)**

- 23. Kumar P, Rayalu S and Dhopte SM, Flyash based zeolite-A suitable sorbent for lead removal, *Indian journal of chemical technology*, 11, 227-233, (2004)
- 24. Somerset VS, Petrik LF, White RA, Klink MJ, Key D and Iwuoha EI, Alkaline hydrothermal zeolites synthesized from high SiO₂ and Al₂O₃ co-disposal fly ash filtrates, *Fuel*, **84**, 2324-2329, (**2005**)
- 25. Bakharev T, Geopolymeric materials prepared using Class F fly ash and elevated temperature curing, *Cement and concrete research*, **35**, 1224-1232, (**2005**)
- **26.** Moriyama R, Takeda S, Onozaki M, Katayama Y, Fukuda KT, Sugihara H and Tani Y, Large-scale synthesis of artificial zeolite from coal fly ash with a small charge of alkaline solution, *Fuel*, **84**, 1455-1461 (**2005**)
- 27. Udhoji JS, Bansiwal AK, Meshram SU and Rayalu SS, Improvement in optical brightness of fly ash based zeolite- A for use as detergent builder, *Journal of Scientific and Industrial research*, **64**, 367-371, (**2005**)
- **28.** Tanaka H, Eguchi H, Fujimoto S and Hino R, Two-step process for synthesis of a single phase Na-A zeolite from coal fly ash by dialysis, *Fuel*, **85**, 1329-1334 (**2006**)
- **29.** Moutsatsou A., Stamatakis E., Hatzitzotzia K. and Protonotarios V., The utilization of Ca-rich and Ca-Sirich fly ashes in zeolites production, *Fuel*, **85**, 657-663 (**2006**)
- **30.** Chen J., Kong H., Wu D, Hu Z., Wang Z. and Wang Y., Removal of phosphate from aqueous solution by zeolite synthesized from fly ash, *Journal of Colloid and Interface Science*, **300**, 491-497, (**2006**)
- **31.** Tanaka H, Fujii A, Fujimoto S and Tanaka Y, Microwave-Assisted Two-Step Process for the Synthesis of a Single-Phase Na-A Zeolite from Coal Fly Ash, *Advanced Powdered Technology*, **19**, 83-94 (**2008**)
- **32.** Wang CF, Li JS, Wang LJ and Sun XY, Influence of NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method, *Journal of Hazardous Materials*, **155**, 58-64 (**2008**)
- **33.** Wu D, Sui Y, Chen X, He S, Wang X and Hainan Kong, Changes of mineralogical-chemical composition, cation exchange capacity, and phosphate immobilization capacity during the hydrothermal conversion process of coal fly ash into zeolite, *Fuel*, **87**, 2194-2200, (**2008**)
- 34. Fotovat F, Kazemian H and Kazemeini M, Synthesis of Na-A and faujasitic zeolites from high silicon fly ash, *Materials Research Bulletin*, 44, 913-917, (2009)
- 35. Belviso C, Cavalcante F and Fiore S, Synthesis of zeolite

from Italian coal fly ash: Differences in crystallization temperature using seawater instead of distilled water, *Waste Management*, **30**, 839-847, (**2010**)

- **36.** Gross-Lorgouilloux M, Soulard M, Caullet P, Patarin J, Moleiro E and Saude I, Conversion of coal fly ashes into faujasite under soft temperature and pressure conditions Influence of additional silica, *Microporous and Mesoporous Materials*, **127**, 41-49, (**2010**)
- **37.** Gross-Lorgouilloux M, Caullet P, Soulard M, Patarin J, Moleiro E and Saude I, Conversion of coal fly ashes into faujasite under soft temperature and pressure conditions Mechanisms of Crystallization, *Microporous and Mesoporous Materials*, **131**, 407-417, **(2010)**
- 38. Medina A, Gamero P, Almanza JM, Vargas A, Montoya A, Vargas G and Izquierdo M, Fly ash from a Mexican mineral coal. II. Source of W zeolite and its effectiveness arsenic (V) adsorption, *Journal of Hazardous Materials*, 181,91-104, (2010)
- **39.** Oh JE, Moon J, Mancio M, Clark SM, Paulo JM and Monteiro P, Bulk modulus of basic sodalite, Na8[AlSiO4]6 (OH)2·2H2O, A possible zeolitic precursor in coal-fly-ash-based geopolymers, *Cement and Concrete Research*, **41**, 107-112 (**2011**)
- Juliana de, Izidoro C, Fungaro DA, Santos F and Wang S, Characteristics of Brazilian coal fly ashes and their synthesized zeolites, *Fuel Processing Technology*, 97, 38-44 (2012)
- **41.** Musyoka NM, Petrik LF, Hums E, Baser H and Schwieger W, In situ ultrasonic monitoring of zeolite A crystallization from coal fly ash, *Catalysis Today*, **190**, 38-46 (**2012**)
- **42.** Belviso C, Cavalcante F, Huertas FJ, Lettino A, Ragone P and Fiore S, The crystallization of zeolite (X- and A-type) from fly ash at 25°C in artificial sea water, *Microporous and Mesoporous Materials*, **162**, 115-121 (**2012**)
- **43.** Thuadaji P and Nuntiya A, Preparation and Characterization of Faujasite using Fly Ash and Amorphous Silica from Rice Husk Ash, *Procedia Engineering*, **32**, 1026-1032 (**2012**)
- 44. Li Q, Xu H, Li F, Li P, Shen L. and Zhai J, Synthesis of geopolymer composites from blends of CFBC fly and bottom ashes, *Fuel*, 97, 366-372 (2012)
- **45.** Mackinnon IDR, Millar GJ and Wanda S.W., Hydrothermal syntheses of zeolite N from kaolin, *Applied Clay Science*, **58**,1-7, (**2012**)
- **46.** Chareonpanich M, Jullaphan O and Tang C, Bench-scale synthesis of zeolite A from sub bituminous coal ashes

with high crystalline silica content, *Journal of Cleaner Production*, **63**, 58–63 (**2011**)

- **47.** Mezni M, Hamzaoui A, Hamdi N and Srasra E, Synthesis of zeolites from the low-grade Tunisian natural illite by two different methods, *Applied Clay Science*, **52**, 209-218 (**2011**)
- 48. Vongvoradit P Worathanakul, Fast Crystallization of SUZ-4 Zeolite with Hydrothermal Synthesis: Part I Temperature and Time Effect, *Procedia Engineering*, 32, 198-204 (2012)
- **49.** Sun M, Hunt HK, Lew CM, Cai R, Liu Y and Yan Y, A Dynamic Organic Structuring-Directing Agent for Pure-Silica-Zeolite AST and LTA Syntheses, *Chinese Journal of Catalysis*, **33**, 85-91 (**2012**)
- **50.** Kucęba IM, A simple thermogravimetric method for the evaluation of the degree of fly ash conversion into zeolite material, *Journal of Porous Materials*, DOI 10.1007/s10934-012-9610-1, (**2012**)
- **51.** Shoumkova A and Stoyanova V, Zeolites formation by hydrothermal alkali activation of coal fly ash from thermal power station "Maritsa 3", Bulgaria, *Fuel*, **103**, 533-541 (**2013**)
- **52.** Wdowin M, Franus M, Panek R, Badura L and Franus W, The conversion technology of fly ash into zeolites. *Clean Techn Environ Policy*, DOI 10.1007/s10098-014-0719-6, (**2014**)
- **53.** Ahmad Shamshad, Fulekar M.H. and Pathak Bhawana, Impact of Coal Based Thermal Power Plant on Environment and its Mitigation Measure, *Int. Res. J. Environment Sci.*, **1**(**4**), 60-64 (**2012**)
- 54. Kumar Saroj, Mishra A.K., Upadhyay M., Singh D., Mishra M. and Kumar Sujata, Kinetic, Thermodynamic and Equilibrium Study on Removal of Lead(II) from Aqueous Solution Using Fly Ash, *Int. Res. J. Environment Sci.*, 3(2), 83-92 (2014)
- 55. Khadse Shaila, Panhekar Deepa and Patil Pralhad, Synthesis of zeolite using fly ash and its application in removal of Cu²⁺, Ni²⁺, Mn²⁺ from Paper Industry Effluent, *Research Journal of Chemical Sciences*, 4(3), 5-9 (2014)
- 56. Singh B.K. and Nema Pragya, Kinetics and Mechanism of removal of Phenol from Aqueous Solutions with Fly ash, *Res. J. Chem. Sci.*, 5(1), 78-82 (2015)
- **57.** Malarvizhi T.S., Santhi T and Manonmani S., A Comparative Study of Modified Lignite Fly Ash for the Adsorption of Nickel from Aqueous Solution by Column and Batch Mode Study, *Res. J. Chem. Sci.*, **3**(2), 44-53 (2013)