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Synthesis of Zeolite from Waste Fly Ash by Using Different Methods

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Zeolites are microporous and aluminosilicate minerals. Two methods have been evaluated for the synthesis of zeolites using waste fly ash as a raw material. First method consists of a combination of fusion of fly ash with NaOH, then hydrothermal treatment, where the fusion product is mixed with water. Second method comprises, initially a conventional hydrothermal technique in which fly ash is treated with NaOH solution at 90 °C for 6 h, followed by filtration and addition of NaOH-$NaAlO_2$ solution into the residual solution. The white precipitate thus formed is subjected to hydrothermal crystallization. The products formed have been characterized using XRF, XRD, SEM and cation exchange capacity. The zeolite formed by first method was composed of zeolite Na-X, hydroxylsodalite and Na-A and second method as a mixture of zeolite Na-X and NaP1. Zeolite samples exhibited much greater cation exchange capacity than raw fly ash and can be used in different applications.

Keywords: Fly ash, Fly ash zeolites, Cation exchange capacity.

INTRODUCTION

Huge amount of coal fly ash generated from electric power plants is a serious waste management problem throughout the world. A small amount out of total generated fly ash is used in building materials such as cement, concrete related applications while the rest is disposed of in landfills leading to various environmental problems such as soil pollution, groundwater pollution, *etc*. Thus, the disposal of such a huge quantity of coal ash has become a critical issue. Therefore, development of novel methods of utilization of the waste fly ash is desirable, either to reduce the cost of disposal or to minimize the environmental impacts.

As fly ash contains high percentage of silica, alumina and some minerals such as quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), hematite (Fe_2O_3), *etc*., they serve as the most suitable and convenient raw material for the synthesis of zeolites. Also, zeolites are very useful material for a wide range of applications such as ion exchangeable materials, molecular sieves, adsorbents and catalysts [1]. Therefore, converting coal fly ash into zeolite is expected to resolve the problem of disposal of fly ash at least partially and thereby minimize its impact on environment. Holler and Wirsching [2] investigated zeolite formation by alkaline activation of fly ash as a function of temperature, solution composition and concentration in open and closed systems and the results showed that zeolite formation depended on the reaction conditions. After that different types of zeolite had been synthesized from coal fly ash by many researchers by different methods such as zeolite A [3-13], zeolite X [3,9,10,11,13-15] zeolite NaP1 [13,16-19], hydroxysodalite [20] and phillipsite [21].

Henmi [20] synthesized hydroxyl-sodalite by conventional hydrothermal process in the temperature range 80-90 °C for 3 to 24 h. The result showed that about 30 % of hydroxyl-sodalite included in the fly ash with high cation exchange capacity compared to the original fly ash. Shigemoto *et al*. [9,10] adopted a method of fusion of fly ash with sodium hydroxide before hydrothermal crystallization and successfully synthesized a single-phase zeolite Na-X or A. Chang and Shih [3] also used a fusion process for the synthesis of zeolite X from different fly ashes with a wide range of chemical compositions. Chang and Shih [4] prepared a single phase Na-A zeolite or a mixture of zeolite A and X, by the addition of aluminium hydroxide to the fused fly ash solution followed by hydrothermal treatment at 60 °C. Hollman *et al*. [11] presented a two-stage synthesis method to produced pure zeolite Na-A and Na-X from initial solution prepared from fly ash. The initial solution was obtained from extracting silica by alkaline attack of fly ash and by adjusting the Si/Al ratio with the addition of Al source. The prepared initial solution was crystallized under static condition during hydrothermal treatment. Rayalu *et al*. [22] investigated the effect of fusion reaction parameters such

as ratio of alkali to fly ash, fusion temperature and crystallization time. The result showed that zeolite Y would be obtained with the alkali:fly ash of 6:5, fusion temperature of 600 °C and crystallization time of 3.5 h. Tanaka *et al*. [5] synthesized pure form and single phase zeolite Na-A from waste solutions by addition of NaOH-$NaAlO_2$ solutions and then aging the solution at 85 °C. Tanaka *et al*. [6] synthesized pure zeolite A from fly ash by a dialysis process using a semipermeable membrane tube. In this process the fly ash was mixed with NaOH-$NaAlO_2$ solution to obtain a homogeneous mixture and this was then added into a semipermeable membrane tube and aged in same NaOH-$NaAlO_2$ solution at 85 °C for 24-30 h. Ojha *et al*. [14] also reported synthesis of zeolite X by alkali fusion followed by hydrothermal treatment. In this method zeolite X was obtained at NaOH/fly ash ratio of 1.3; fusion temperature 550 °C; aging time 24 h and 6 h of hydrothermal treatment. Hui and Chao [7] synthesized pure form, single phase and high crystalline zeolite 4A by applying a step-change of synthesis temperature during hydrothermal treatment to reduce the overall synthesis time. Wang *et al*. [12] investigated the influence of NaOH concentration on synthesis of pure form of zeolite A from fly ash using a two stage method, first to dissolve silica from fly ash with NaOH and then with the addition of Al source to prepare initial gel. Belviso *et al*. [15] investigated the synthesis of zeolite X from coal fly ash by a process of hydrothermal activation after a pre-treatment fusion with NaOH. In this study, a 1:1.2 ratio of fly ash/NaOH was ground and fused at 560 °C for 1h and then mixed with 43 mL of distilled water and seawater, separately and then incubated for 4 days at a temperature between (35-40 °C). The result showed that zeolite X synthesized was higher in seawater as crystallizing agent than using distilled water. Rios *et al*. [23] compared the two methods of zeolite formation; i) by hydrothermal treatment in NaOH and KOH and ii) by fusion with NaOH followed by hydrothermal reaction. The result shows that by hydrothermal treatment, Na-phillipsite, hydroxylsodalite, zeolite K-F with traces of tobermonite and analcime zeolite Linde type F and herschelite were obtained. Whereas by alkaline fusion, faujasite and cancrinite were obtained with NaOH as an activator, while no zeolitic material was crystallized using KOH. Kazemian *et al*. [19] reported that after alkaline fusion, addition of sodium aluminate to fly ash also induced NaP1 zeolite at 120 °C for 4 h. Lee and Jo [13] also synthesized zeolite from coal fly ash through hydrothermal treatment at various ratios of NaOH/fly ash and $NaAlO_2$/fly ash, including an initial alkali fusion step and reported that zeolite NaP1 was formed with a NaOH/fly ash ratio of 0.5 and Na-A with a $NaAlO_2$/fly ash ratio of 0.53 at a reaction temperature of 100 °C.

Taking all these observation into account, in the work presented here we adopted two methods of zeolite preparation and the products were compared in terms of ion exchange capacity and structural characteristics.

EXPERIMENTAL

Coal fly ash was obtained from Chandrapur super thermal power plant of Maharashtra State Electricity Board, Maharashtra, India. Before any treatment, the raw fly ash samples were bench dried. The unburnt carbon and other volatile materials present in the fly ash were removed by calcination at 800 °C for 1 h.

The chemical composition of fly ash and fly ash zeolite was determined by X-ray fluorescence (XRF) using a Philips MagiX PRO, Model PW 2440, wavelength dispersive X-ray fluorescence spectrometer. Samples mineralogy was determined by X-ray diffraction (XRD) analysis using a Bruker 8 D advanced X-ray diffractometer. Photo-micrographs of fly ash and synthesized zeolite were obtained using a Hitachi Model S-3400N scanning electron microscope (SEM). The cation exchange capacity of both the raw fly ash and zeolitized material was determined using the ammonium acetate method using Indian Standard: 2720 [24] and ammonium adsorption capacity was determined using ammonium chloride solution containing 386 ± 5 ppm of equivalent NH_4^+ concentration. One gram of sample was placed in a 250 mL conical flask, to which 100 mL of NH_4^+ solution was added and the flask was shaken in a rotary shaker to achieve equilibrium. The solutions were filtered and then analyzed for ammonia using Kjeldahl distillation followed by acidimetric titration (APHA 1992) [25].

Zeolite formation by silica extraction method: In this method, 40 g of fly ash was added into 400 mL of 2 M NaOH in Teflon digestion bombs. The slurry thus prepared was aged in an oven at 90 °C for 6 h without stirring. The solution was separated from the mixture by filtration and the volume obtained was about 350 mL. NaOH-$NaAlO_2$ solution was prepared by vigorously mixing 8 g $NaAlO_2$ in 100 mL 2M NaOH solution. Then, 100 mL of a mixture of NaOH-$NaAlO_2$ solution was added to 300 mL solution obtained at first stage and the solution obtained was stirred for 0.5 h at room temperature. The precipitate formed was aged in an oven at 90 °C for 8 h without stirring. The materials obtained were filtered, washed repeatedly with deionized water until the pH of the washing reached 8-9 and then dried in an oven at 45-50 °C.

Zeolite formation by fusion method: In this method 40 g of fly ash and 60 g NaOH were crushed and then heated in a platinum crucible at 600 °C for 1 h. The fused mixture obtained was cooled to room temperature, crushed again and dissolved in 400 mL distilled water. This solution was aged for 8 h at room temperature with stirring. After aging, the sample was placed at 100 °C for 12 h in an oven. Thereafter, the sample was filtered, washed several times with deionized water and dried at 45-50 °C.

RESULTS AND DISCUSSION

The chemical composition determined by XRF analysis of Chandrapur fly ash and prepared zeolites is shown in Table-1. The result shows that fly ash contained 58.94 % SiO_2 and 22.78 % Al_2O_3 which make them suitable for zeolite synthesis. Other important parameters for zeolite synthesis are SiO_2:Al_2O_3 ratio. The SiO_2:Al_2O_3 ratio in the fly ash sample was 2.59. The decrease in SiO_2 percentage in fly ash sample as they were transformed into zeolites indicates that dissolution of SiO_2 had taken place during alkaline hydrothermal treatment. The increase in Na_2O content from 0.31 % in fly ash to 33.2 % and 26.61 % in transformed zeolites shows that conversion to Na zeolites has taken place as Na has been incorporated in the structure of zeolite. The Al_2O_3 content in zeolite indicates

TABLE-1
CHEMICAL COMPOSITION OF FLY ASH AND PREPARED ZEOLITE (wt %)

Component	Fly ash	Zeolite by silica extraction method	Zeolite by fusion method
SiO_2	58.94	39.84	35.80
Al_2O_3	22.78	25.78	21.24
Na_2O	0.31	33.2	26.61
Fe_2O_3	10.49	0.11	10.55
K_2O	1.35	1.07	0.56
Ti	2.00	–	2.35
CaO	1.94	–	1.69
MgO	0.98	–	0.89
P_2O_5	0.88	–	0.06
SO_3	0.18	–	0.08
Sr	0.05	–	0
Zr	0.09	–	0.07
Cl	–	–	0.08

that part of it is converted into zeolite and rest remains in unreacted mullite phase of the fly ash. Prepared zeolites were characterized without separation and purification. The alumino-silicate glass of the fly ash forms the source material for zeolite synthesis.

XRD analysis of fly ash and fly ash zeolites: XRD analysis was conducted to determine the crystalline phases present in both raw fly ash and zeolites which were prepared by silica extraction and by fusion method is shown in Fig. 1. Fig. 1a shows that the predominant crystalline phases present in the fly ash are quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$). Figs. 1b and 1c show that a more crystalline zeolite phase has been formed during both methods of zeolite formation. The decrease in quartz peak height in the zeolite phase indicates that this mineral has been dissolved in alkaline medium at high temperature and pressure. The XRD patterns of the zeolite synthesized from fly ash by silica extraction method indicate the formation of zeolite X and NaP1, as shown in Fig 1b. Fig. 1c shows XRD pattern of zeolite synthesized by fusion method and it indicates that the product formed is a mixture of zeolite X, hydroxysodalite and zeolite A.

Morphological analysis of fly ash and fly ash zeolites: Fig. 2 shows the scanning electron microscope images of fly

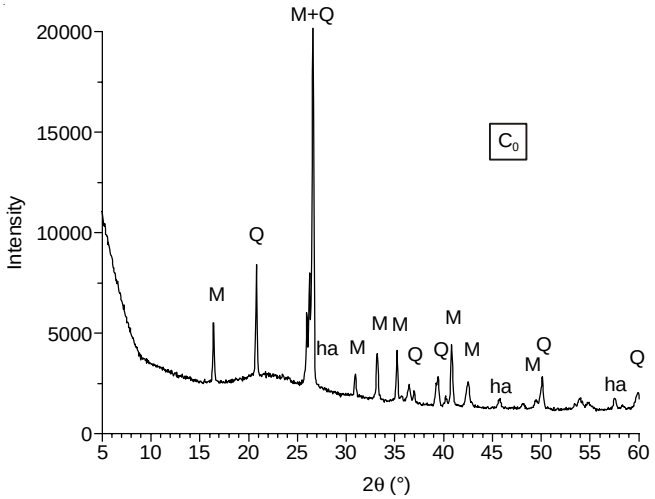

Fig. 1a. XRD pattern of the unmodified fly ash sample; where M = Mullite, Q = Quartz and ha = Halide

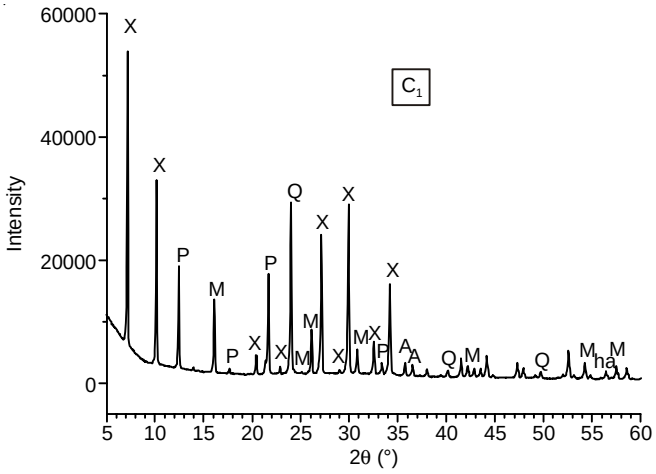

Fig. 1b. XRD pattern of the Zeolites prepared from fly ash by silica extraction method; where X = zeolite Na-X, P = Zeolite Na-P1, M= Mullite, Q = Quartz and ha = Halide

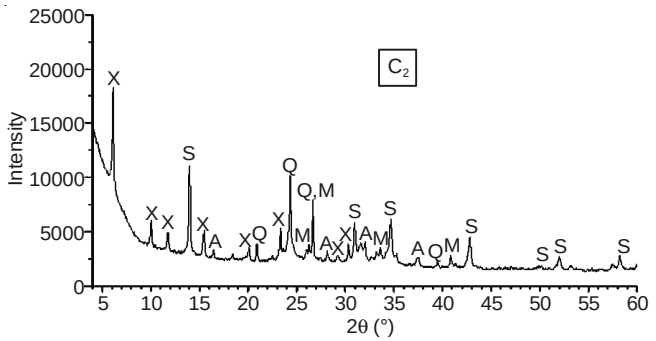

Fig. 1c. XRD pattern of the Zeolites prepared from fly ash by fusion method; where X = zeolite Na-X, S = hydroxylsodalite, A = Zeolite Na-A, M = Mullite and Q = Quartz

ash particles and prepared zeolites. The fly ash particles are spherical in nature and have a smooth surface due to a covering of alumino-silicate glass. In Fig. 2b, by silica extraction method, mixed phases of zeolite X and NaP1, both cubic and octahedral crystals are seen. The Na–A and Na–X zeolites possess the LTA and FAU type framework respectively. Therefore, the morphology of the Na–A and Na–X zeolites generally exhibits respectively cubic and octahedral particles [26]. Almost similar results were shown by several researchers [5,11,12,27]. By fusion method of zeolite formation, the absence of spherical particles and the development of rough surfaces and crystals formed in treated fly ash indicate that zeolite is formed on the surface of the fly ash particles as a result of hydrothermal treatment. Fig. 2c indicates the formation of mixed phases of zeolite X, zeolite A and hydroxysodalite. These results are similar to those reported by several researchers [8,10,28].

Cation exchange capacity of fly ash and prepared zeolites: The Chandrapur fly ashes had a cation exchange capacity of 5.9 meq/100 g, while zeolite prepared by fusion method has increased this to 229 meq/100 g whereas zeolite prepared by silica extraction method has increased this to 421 meq/100 g (Fig. 3). The high cation exchange capacity of prepared zeolites suggests that the original fly ash sample has an optimum Si: Al ratio for the formation of zeolites that the precise mineral association of the Si and Al alumino-silicate glass is ideal for transformation [17].

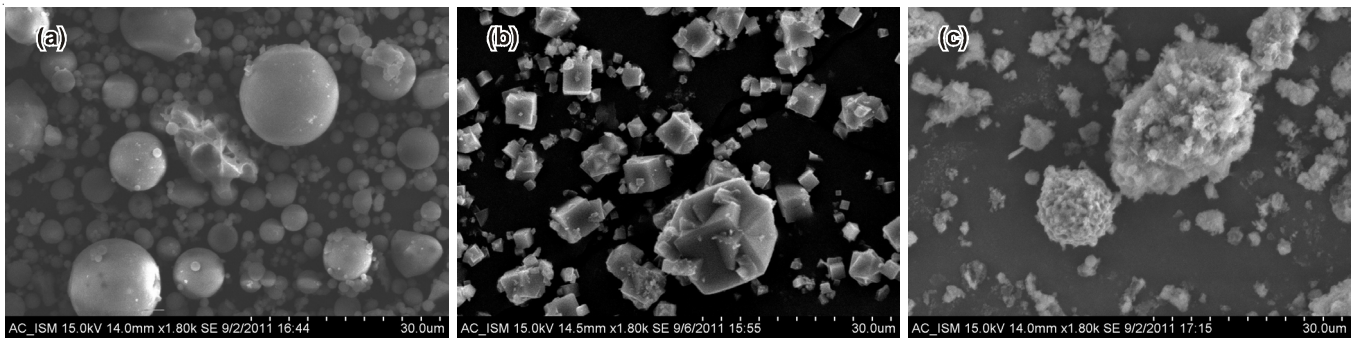

Fig. 2. (a) Chandrapur fly ash particles, (b) Formation of zeolite by silica extraction method and (c) Formation of zeolite by fusion method on fly ash particle

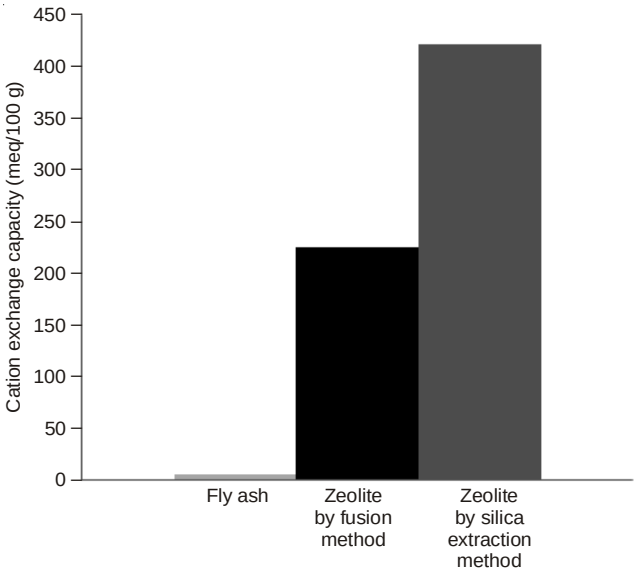

Fig. 3. Cation exchange capacity of fly ash and prepared zeolites

Ammonium adsorption capacity of fly ash and prepared zeolites: Results obtained from ammonium adsorption tests performed on raw fly ash and their zeolitic products obtained using different methods are shown in Fig. 4.

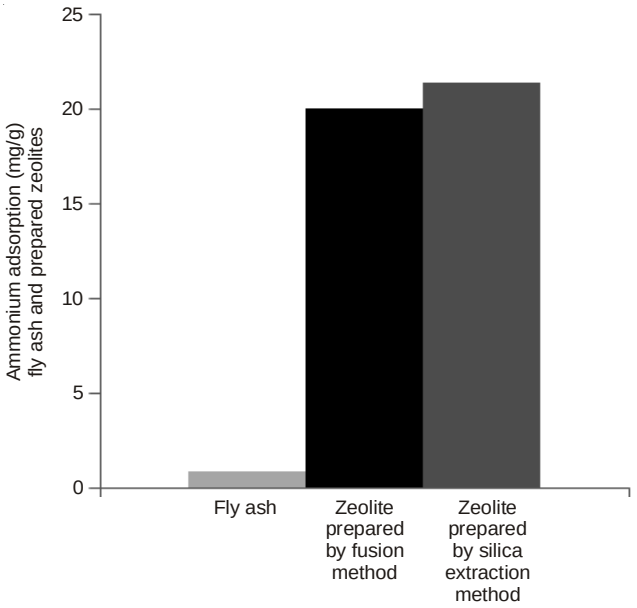

Fig. 4. Ammonium adsorption capacity of fly ash and prepared zeolites

Ammonium retention by raw fly ash was 0.86 mg of NH_4^+/g of fly ash. Zeolites prepared by fusion method and by silica extraction method have shown high retention capacity for ammonium ions, 20.08 and 21.46 mg NH_4^+/g, respectively. The high ammonium adsorption capacity of the prepared zeolites suggests that the zeolites have potential application as sorbents of NH_4^+ ion from wastewaters, such as those arising from farming activities or landfill leachate [29]. Once the ammonium ion is retained in the zeolites, the resulting product could be used as a soil conditioner because the release of NH_4^+ cation from the zeolites is very slow [30].

Conclusion

The conversion of coal fly ash into zeolites could contribute to the enhancement of waste utilization in a high-value application. In the present work, two methods (silica extraction and fusion) have been evaluated for the synthesis of zeolites using fly ash as a raw material. The prepared zeolite samples exhibited greater cation exchange capacities and ammonium adsorption capacities than raw fly ash. This high cation exchange capacity and ammonium adsorption capacity makes the prepared zeolites as a suitable material in many environmental applications. The material formed by silica extraction method was identified as mixed phases of zeolite X and NaP1. These zeolitic minerals have application in adsorption and separation processes, purification of water, wastewater and soil remediation and in adsorption of industrial gases [31]. Mixed phases of zeolite X, A and hydroxysodalite was formed in fusion method. These zeolites have special application in drying of gases and liquids, washing builder and separation of normal from branched paraffins [6] and production of ultra-pure water by desalination of sea water using hydroxy sodalite membrane [20]. Hence, synthesis of zeolite from coal fly ash would be of dual advantage, as it would make use of fly ash and utilizes it for the solving various environmental problems.

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REFERENCES

1. D.W. Breck, Zeolite Molecular Sieves, John Wiley & Sons, New York (1974).
2. H. Hollar and U. Wirsching, *Fortschr. Miner.*, **63**, 21 (1985).
3. H.L. Chang and W.H. Shih, *Ind. Eng. Chem. Res.*, **39**, 4185 (2000).
4. H.L. Chang and W.H. Shih, *Ind. Eng. Chem. Res.*, **37**, 71 (1998).
5. H. Tanaka, Y. Sakai and R. Hino, *Mater. Res. Bull.*, **37**, 1873 (2002).
6. H. Tanaka, A. Miyagawa, H. Eguchi and R. Hino, *Ind. Eng. Chem. Res.*, **43**, 6090 (2004).
7. K.S. Hui and C.Y.H. Chao, *Micropor. Mesopor. Mater.*, **88**, 145 (2006).
8. S.S. Rayalu, J.S. Udhoji, K.N. Munshi and M.Z. Hasan, *J. Hazard. Mater.*, **88**, 107 (2001).
9. N. Shigemoto, S. Shirakami, S. Hirano and H. Hayashi, *Nippon Kagaku Kaishi*, **5**, 484 (1992).
10. N. Shigemoto, H. Hayashi and K. Miyaura, *J. Mater. Sci.*, **28**, 4781 (1993).
11. G.G. Hollman, G. Steenbruggen and M. Janssen-Jurkovicová, *Fuel*, **78**, 1225 (1999).
12. C.F. Wang, J.S. Li, L.J. Wang and X.Y. Sun, *J. Hazard. Mater.*, **155**, 58 (2008).
13. K.M. Lee and Y.M. Jo, *J. Mater. Cycles Waste Manage.*, **12**, 212 (2010).
14. K. Ojha, N.C. Pradhan and A.N. Samanta, *Bull. Mater. Sci.*, **27**, 555 (2004).
15. C. Belviso, F. Cavalcante, A. Lettino and S. Fiore, *Coal Combust. Gasificat. Prod.*, **1**, 7 (2009).
16. M. Inada, Y. Eguchi, N. Enomoto and J. Hojo, *Fuel*, **84**, 299 (2005).
17. V. Berkgaut and A. Singer, *Appl. Clay Sci.*, **10**, 369 (1996).
18. N. Murayama, H. Yamamoto and J. Shibata, *Int. J. Miner. Process.*, **64**, 1 (2002).
19. H. Kazemian, Z. Naghdali, T.G. Kashani and F. Farhadi, *Adv. Powder Technol.*, **21**, 279 (2010).
20. T. Henmi, *Soil Sci. Plant Nutr.*, **33**, 517 (1987).
21. M. Park and J. Choi, *Clay Sci.*, **9**, 219 (1995).
22. S. Rayalu, S.U. Meshram and M.Z. Hasan, *J. Hazard. Mater.*, **77**, 123 (2000).
23. C.A. Ríos R, C.D. Williams and C.L. Roberts, *Fuel*, **88**, 1403 (2009).
24. Indian Standard: 2720 (Part XXIV), Methods of Test for Soils, Determination of Cation Exchange Capacity, Bureau of Indian Standard, New Delhi.
25. APHA, AWWA and WEF, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, edn 18 (1992).
26. H. Tanaka, H. Eguchi, S. Fujimoto and R. Hino, *Fuel*, **85**, 1329 (2006).
27. W.N. Majchrzak-Kuceba and W. Nowak, *Thermochim. Acta*, **437**, 67 (2005).
28. A. Molina and C. Poole, *Miner. Eng.*, **17**, 167 (2004).
29. Y. Luna, E. Otal, L.F. Vilches, J. Vale, X. Querol and C.F. Pereira, *Waste Manage.*, **27**, 1877 (2007).
30. B. Prasad, S. Maity, K. Sangita, A.K. Mahato and R.J.G. Mortimer, *Environ. Technol.*, **33**, 37 (2012).
31. X. Querol, J.C. Umaña, F. Plana, A. Alastuey, A. Lopez-Soler, A. Medinaceli, A. Valero, M.J. Domingo and E. Garcia-Rojo, *Fuel*, **80**, 857 (2001).