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Characterization, Structural Identification and Environmental Applications of Flyash Based Zeolite

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Relatively pure zeolite-A phases have been synthesized from flyash. The formation of these relatively pure phases having wide ranged environmental application is substantiated by detailed structural identification and characterization of flyash based zeolite-A (FAZ-A) using X-ray diffraction (XRD) method. Absolute crystallinity of zeolite-A sample has been determined along with identification of crystalline and amorphous phases. The X-ray pattern of FAZ-A has been compared with commercial standard zeolite-A procured from Degussa. The as-synthesized FAZ-A has been applied for targeting cationic pollutants, *viz.*, ammonium ion and heavy metals (Pb, Cd, Cu) through cation exchange which shows comparable efficiency with commercial samples.

Key Words: Zeolite-A, XRD, Flyash, Characterization, Synthesis.

INTRODUCTION

XRD provides information on long-range order and is a recognized method for identifying crystalline materials by comparing the *d*-spacing and intensity of diffraction peaks with those of standard samples. Z. Fengqi *et al.*[1] gave a method for measuring the absolute crystallinity of zeolite-A using XRD pattern. They proposed that the diffraction peaks of the crystalline and amorphous phase in the diffraction pattern could also be isolated. The computer simulated XRD pattern can also be used in zeolite research. Modern powder diffraction consists of several computer programs for calculation of diffraction patterns using the results of structural analysis. The comparison between calculated and measured X-ray diffraction pattern gives valuable information about the correctness of atom location in the crystal structure. NaA type zeolite-A was chosen as an example by W. Schmitz[2] to show the possibilities of such programs in zeolite research. Tai *et al.*[3] used the X-ray crystallographic data for calculating intraframe work potential function of zeolites.

This paper reports the structural aspects of zeolite-A sample from flyash pertaining to crystallinity and other related parameters using XRD as a technique.

EXPERIMENTAL

Materials: Sub-bituminous based flyash was collected from the electrostatic hopper of thermal power plant at Koradi. The zeolite samples designated as FASBC-1 to FASBC-5 have been synthesized under different reaction conditions and are detailed in Table-1. The zeolite samples have been synthesized using the reported process and patented elsewhere[4, 5]. A brief description of the method is as follows:

Synthesis: The flyash based zeolite-A (FAZ-A) sample was synthesized by fusing flyash with sodium hydroxide. A homogeneous fusion mixture was prepared by proper grinding and mixing of flyash and caustic soda in a certain ratio. This mixture was heated to at least 500°C , preferably between 550–600°C for a certain period of time. The resultant fused mass was cooled, milled and mixed thoroughly in distilled water. The slurry was then subjected to aging for a certain period of time. This amorphous aluminosilicate gel was then subjected to crystallization preferably between 90–110°C for about 8–12 h. The solid crystalline product was recovered by filtration and washed thoroughly till the filtrate pH was 10–11 and dried at a temperature of 50–60°C.

Characterization: The X-ray diffraction patterns have been recorded using X-ray diffractometer, Phillips Model PW-1710 atomic diffractometer. The operating target voltage was 35 kV and the current was 20 mA. The radiations of CuK_α of wavelength 1.54056 Å were generated using X-ray generator of model PW-1729 of same make and the β-radiations were filtered using a monochromator. The samples were scanned for the 2θ range 5–50°. The experiment was repeated for zeolite-A standard under exactly identical conditions. The values of interplanar *d*-spacing corresponding to Bragg's reflections (2θ) for zeolite-A as reported in literature are 12.20 ± 0.20, 8.60 ± 0.20, 7.05 ± 0.15, 4.07 ± 0.08, 3.68 ± 0.07, 3.38 ± 0.06, 3.26 ± 05, 2.96 ± 0.05, 2.73 ± 0.05 and 2.60 ± 0.05. These values have been used as a basis for identification and quantification of crystalline phase. For quantification of crystalline zeolite-A phase in the FAZ-A sample, per cent crystallinity and degree of crystallization were calculated as follows:

Per cent crystallinity: The per cent crystallinity of FAZ-A was calculated by comparing the sum of peak intensities for the characteristic '*d*' values of FAZ-A with that of standard zeolite-A considering that the standard zeolite-A is having 100% crystallinity[6].

$$\text{Per cent crystallinity} = \frac{\text{Sum of peak intensities for FAZ-A} \times 100}{\text{Sum of peak intensities for standard zeolite-A}}$$

Degree of crystallization: Degree of crystallization of zeolite-A sample is determined by using X-ray diffraction pattern obtained from X-ray diffraction method. Points of diffraction angle $2\theta = 9°$ and $2\theta = 39°$ in the X-ray diffraction pattern are connected by a straight line. This line is designated as the base line. Two lowermost points in the trough between every two adjacent peaks (except those in which the distance between two diffraction peaks is smaller than 1) are connected by a straight line. This line is designated as the amorphous line. The degree (%) of crystallization is calculated using the formula:

$$\text{Degree of crystallization} = \frac{S_C}{S_A - S_C} \times 100$$

where S_A represents the area between the base line and amorphous line and S_C denotes the area between the amorphous line and the diffraction curve.

Lattice parameters: The XRD data of the FAZ-A samples was subjected to indexing using a Pascal-written program, *i.e.*, XRAYSCAN, which is able to index and refine simultaneously the powder diffraction data containing many spurious peaks. XRAYSCAN finds all possible solutions of lattice parameters through Monte Carlo, or random searching method and refines the raw solutions by Powell's method for the accurate lattice parameters. At the present time, XRAYSCAN is capable of analyzing materials with cubic, tetragonal, hexagonal, tetragonal or orthorhombic structures on an IBM PC.

RESULTS AND DISCUSSION

The X-ray powder diffractograms of FAZ-A samples, *viz.*, FASBC-1, FASBC-2, FASBC-3, FASBC-4 and FASBC-5, and Zeolite-A standard procured from Degussa, Germany have been recorded and shown in Figs. 1, 2, 3, 4, 5 and 6 respectively. These five standard FAZ-A samples synthesized under different reaction conditions along with standard zeolite-A were selected for the detailed structural analysis using XRD technique and the various parameters determined from the XRD data are discussed as follows:

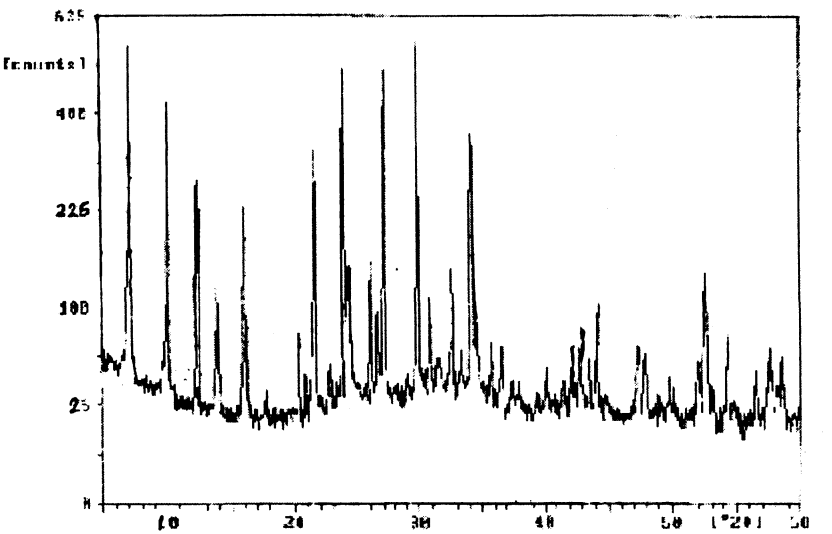

Fig. 1. XRD pattern of FASBC-1

Per cent Crystallinity: The per cent crystallinity values of FASBC-1 to FASBC-5 are reported in Table-1. The FAZ (FASBC-1) synthesized by using 20 mL of sodium aluminate (Na_2O, 50.3%; Al_2O_3, 39%) and unsieved flyash without seeding has 72% crystallinity value, which increases to 85% (FASBC-2) by

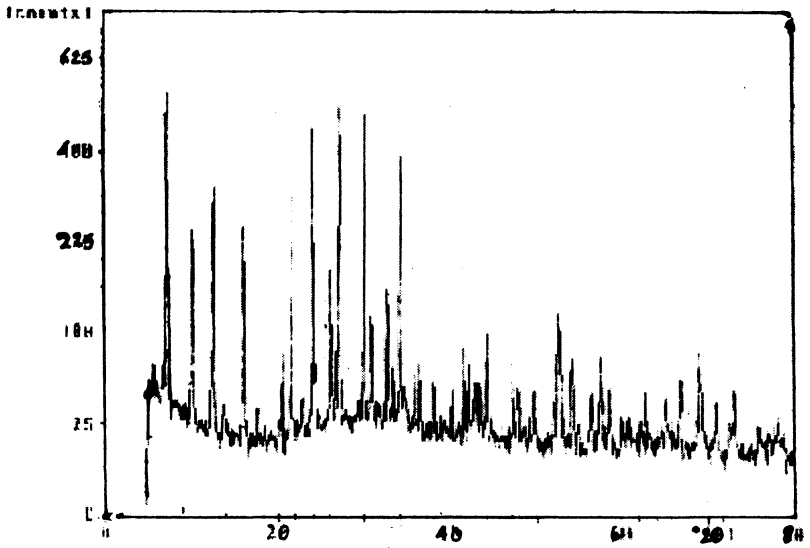

Fig. 2. XRD pattern of FASBC-2

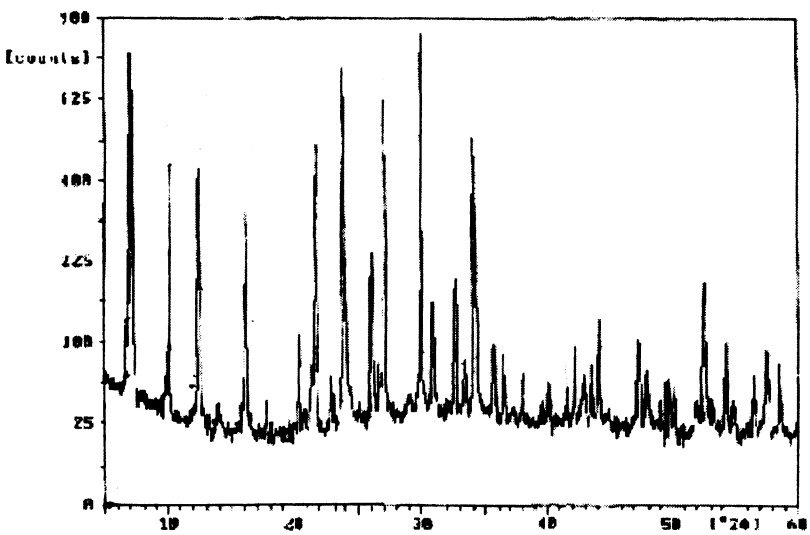

Fig. 3. XRD pattern of FASBC-3

addition of zeolite-A seeding in the slurry before the stirring and aging step. Thus seeding has a pronounced effect on the per cent crystallinity and in turn on the synthesis of FAZ-A[7,8]. The FAZ-A synthesized by using sieved flyash (FASBC-3) of particle size 170 micron shows 100% crystallinity. This shows that sieving of flyash[9] removes almost all the impurities from flyash so as to enable synthesis of 100% crystalline FAZ-A. FASBC-4 synthesized from flyash of particle size 53

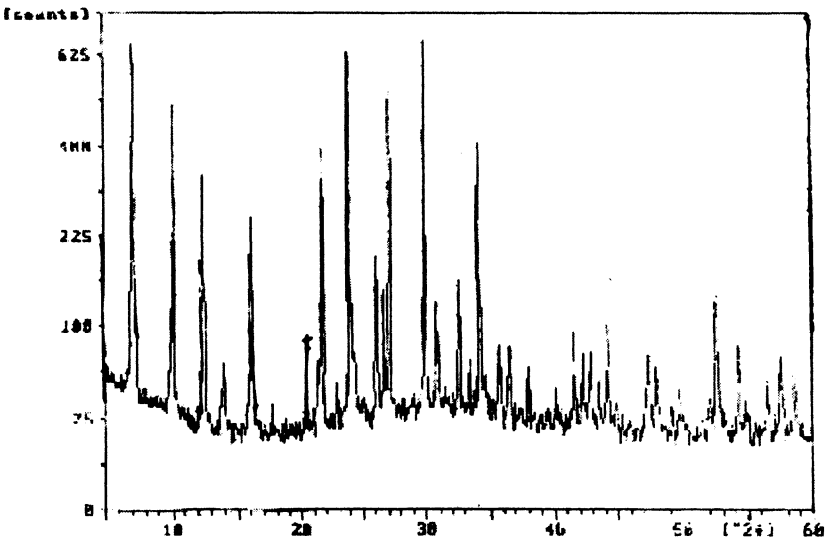

Fig. 4. XRD pattern of FASBC-4

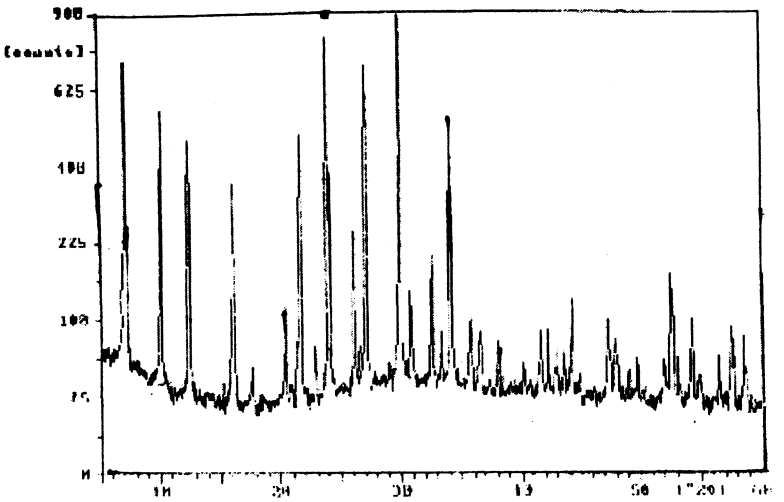

Fig. 5. XRD pattern of FASBC-5

micron also gives 100% crystalline sample. It is thus apparent that sieving to obtain reduced particle size has significant effect on per cent crystallinity. FASBC-5 synthesized from sieved flyash further subjected to magnetic separation and using 42 mL of sodium aluminate (Na_2O, 20.2%; Al_2O_3, 18.4%) shows 100% crystallinity. Thus magnetic separation has no effect on the per cent crystallinity of zeolite-A.

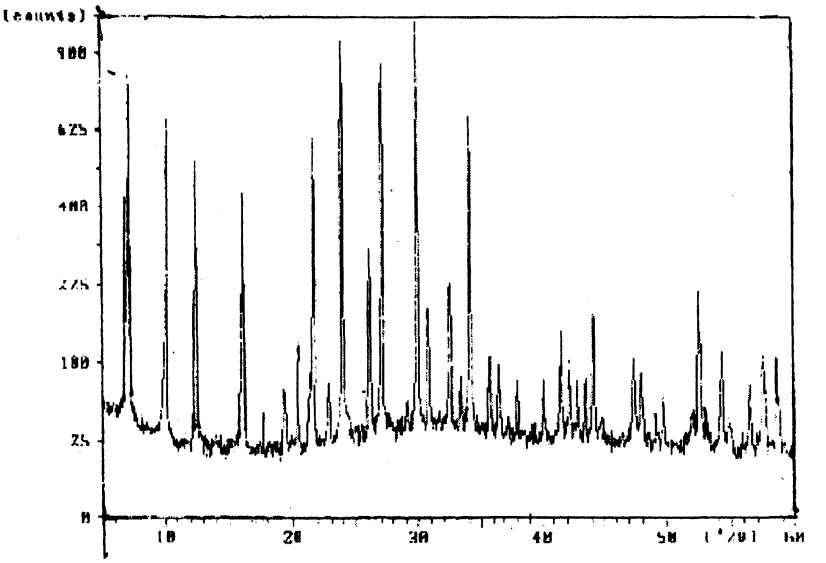

Fig. 6. XRD pattern of standard zeolite-A (Degussa)

TABLE-1
LATTICE PARAMETERS WITH RESPECT TO VARIATION IN EXPERIMENTAL CONDITIONS FOR THE SYNTHESIS OF FAZ-A

Sample	Pre-treatment	Sodium aluminate composition (%)	Sod. aluminate ($NaAlO_2$) mL	Seeding (g)	Crystallization time (h)	Lattice parameters	Degree of crystallisation	Per cent crystallanity
						a = b = c		
FASBC-1		Na_2O: 50.3, Al_2O_3: 39	20	–ve	3.0	24.58	84.93	72
FASBC-2		Na_2O: 50.3, Al_2O_3: 39	20	+ve	3.0	24.58	87.76	85
FASBC-3	Sieving by 130 micron	Na_2O: 50.3, Al_2O_3: 39	20	+ve	3.0	24.60	88.23	100
FASBC-4	Sieving by 53 micron	Na_2O: 50.3, Al_2O_3: 39	20	+ve	3.5	24.59	86.50	100
FASBC-5	Sieving by 53 micron. Magnetic separation. Ferric hydroxide removed from SA-VI	Na_2O: 20.2, Al_2O_3: 18.4	42	+ve	3.0	24.58	88.51	100
Degussa						24.59		100
Theoretical value						24.60		

Degree of crystallization: The degree of crystallization has been calculated as per the reported method elsewhere[10]. The degree of crystallization of FASBC-2 is greater than that of FASBC-1 indicating that seeding has a positive effect on the synthesis of FAZ-A. By comparing the degree of crystallization of FASBC-2 and FASBC-3 it can be observed that there is slight increase in degree of crystallization by sieving the flyash. Usage of flyash of still further reduced particle size through sieving and also incorporation of magnetic separation as a pretreatment step have no significant effect on the degree of crystallization.

The XRD data was also used for determining the structural details for the FAZ-A samples like lattice parameters, Miller indices, etc. The results of lattice parameters obtained by using computer program XRAYSCAN along with the calculations for the FAZ-A samples FASBC-1 to FASBC-5 and standard zeolite-A are tabulated in Tables 2–7 respectively.

TABLE-2
X-RAY DIFFRACTION DATA FOR FASBC-1

2θ	H	K	L	d-cal. Value	d-obs. Value	Δd value	Rel.Int. (%)	2θ cal.	Δθ
7.210	2	0	0	12.2879	12.2809	–0.0070	81.8	7.197	–0.006
10.205	2	2	0	8.6889	8.6824	–0.0065	62.2	10.185	–0.010
12.490	2	2	2	7.0944	7.0987	0.0043	50.9	12.482	–0.004
16.130	4	2	0	5.4953	5.5040	0.0087	37.2	16.136	0.003
17.680	4	2	2	5.0165	5.0248	0.0083	4.0	17.688	0.004
20.445	4	4	0	4.3444	4.3511	0.0067	10.2	20.451	0.003
21.680	6	0	0	4.0960	4.1060	0.0100	56.1	21.707	0.013
22.875	6	2	0	3.8858	3.8941	0.0083	5.5	22.896	0.011
24.010	6	2	2	3.7049	3.7125	0.0076	93.0	24.030	0.010
26.095	6	4	0	3.4081	3.4204	0.0123	28.1	26.159	0.032
27.130	6	4	2	3.2841	3.2923	0.0082	76.8	27.165	0.017
29.950	8	2	0	2.9803	2.9884	0.0081	100.0	29.996	0.023
30.855	8	2	2	2.8963	2.9028	0.0065	19.9	30.887	0.016
32.570	8	4	0	2.7477	2.7538	0.0061	21.4	32.603	0.017
33.375	8	4	2	2.6814	2.6892	0.0078	9.7	33.432	0.028
34.165	6	6	4	2.6198	2.6288	0.0090	61.6	34.242	0.039
35.745	8	4	4	2.5083	2.5161	0.0078	8.9	35.815	0.035
36.510	8	6	0	2.4576	2.4651	0.0075	8.9	36.580	0.035
38.020	6	6	6	2.3648	2.3706	0.0058	6.5	38.069	0.024

Type of crystal system = cubic; Lattice parameters: a = b = c = 24.58 Å; α = β = γ = 90°; Volume of unit cell = 14850.65 Å.

TABLE-3
X-RAY DIFFRACTION DATA FOR FASBC-2

2θ	H	K	L	d-cal. Value	d-obs. Value	Δd value	Rel.Int. (%)	2θ cal.	Δθ
7.205	2	0	0	12.2900	12.2894	–0.0005	89.9	7.196	–0.005
10.190	2	2	0	8.6903	8.6952	0.0049	78.8	10.183	–0.003
12.490	2	2	2	7.0956	7.0987	0.0031	45.2	12.480	–0.005
13.975	4	0	0	6.1450	6.3475	0.2025	16.8	14.420	0.223
16.135	4	2	0	5.4962	5.5023	0.0061	41.2	16.133	–0.001
17.680	4	2	2	5.0174	5.0248	0.0074	3.1	17.685	0.002
20.465	4	4	0	4.3452	4.3469	0.0017	11.0	20.448	–0.009
21.690	6	0	0	4.0967	4.1041	0.0075	58.9	21.703	0.006
22.845	6	2	0	3.8864	3.8991	0.0127	6.7	22.892	0.024
24.000	6	2	2	3.7056	3.7141	0.0085	8.3	24.026	0.013
26.095	6	4	0	3.4086	3.4204	0.0118	26.8	26.155	0.030
27.110	6	4	2	3.2846	3.2946	0.0100	92.4	27.160	0.025
29.955	8	2	0	2.9808	2.9879	0.0071	100.0	29.991	0.018
30.845	8	2	2	2.8968	2.9037	0.0069	17.1	30.882	0.018
32.555	8	4	0	2.7481	2.7550	0.0069	25.4	32.598	0.021
33.410	8	4	2	2.6819	2.6864	0.0045	8.8	33.426	0.008
34.175	6	6	4	2.6202	2.6280	0.0078	64.3	34.237	0.031
34.605	8	5	1	2.5909	2.5963	0.0054	12.8	34.636	0.015
35.765	8	4	4	2.5087	2.5148	0.0061	10.2	35.809	0.022
36.490	8	6	0	2.4580	2.4664	0.0084	8.1	36.573	0.042

TABLE-4
X-RAY DIFFRACTION DATA FOR FASBC-3

2θ	H	K	L	d-cal. Value	d-obs. Value	Δd value	Rel.Int. (%)	2θ cal.	Δθ
7.185	2	0	0	12.2975	12.2930	–0.0045	82.9	7.191	0.003
10.185	2	2	0	8.6956	8.6779	–0.0177	64.6	10.177	–0.004
12.475	2	2	2	7.1000	7.0896	–0.0104	43.7	12.472	–0.001
16.130	4	2	0	5.4996	5.4904	–0.0092	33.8	16.123	–0.003
17.650	4	2	2	5.0204	5.0208	0.0004	2.3	17.674	0.012
20.410	4	4	0	4.3478	4.3477	–0.0001	10.8	20.435	0.013
21.680	6	0	0	4.0992	4.0958	–0.0034	55.9	21.689	0.005
22.865	6	2	0	3.8888	3.8861	–0.0027	4.5	22.878	0.007
24.005	6	2	2	3.7078	3.7041	–0.0037	75.8	24.011	0.003
26.100	6	4	0	3.4107	3.4113	0.0006	24.8	26.138	0.019
27.105	6	4	2	3.2866	3.2871	0.0005	74.6	27.143	0.019
29.935	8	2	0	2.9826	2.9825	–0.0001	100.0	29.972	0.019
30.815	6	6	0	2.8985	2.8993	0.0008	16.7	30.862	0.024
32.545	8	4	0	2.7498	2.7490	–0.0008	19.8	32.577	0.016
33.350	8	4	2	2.6835	2.6844	0.0009	7.4	33.405	0.027
34.170	6	6	4	2.6218	2.6219	0.0001	61.5	34.215	0.022
35.750	8	4	4	2.5102	2.5095	–0.0007	8.9	35.786	0.018
36.500	8	6	0	2.4595	2.4597	0.0002	8.9	36.550	0.025
38.005	6	6	6	2.3667	2.3657	–0.0010	4.2	38.038	0.017
39.470	8	6	4	2.2836	2.2812	–0.0024	1.4	39.478	0.004

Type of crystal system = cubic; Lattice parameters: a = b = c = 24.58 Å; $\alpha = \beta = \gamma = 90°$; Volume of unit cell = 14850.65 Å.

TABLE-5
X-RAY DIFFRACTION DATA FOR FASBC-4

2θ	H	K	L	d-cal. Value	d-obs. Value	Δd value	Rel.Int. (%)	2θ cal.	Δθ
7.205	2	0	0	12.2944	12.2894	–0.0049	92.1	7.193	–0.006
10.190	2	2	0	8.6934	8.6952	0.0018	67.8	10.180	–0.005
16.130	4	2	0	5.4982	5.5040	0.0058	34.2	16.127	–0.001
17.665	4	2	2	5.0191	5.0291	0.0100	2.4	17.678	0.007
20.425	4	4	0	4.3467	4.3553	0.0086	11.9	20.441	0.008
21.695	6	0	0	4.0981	4.1032	0.0051	61.3	21.695	0.000
22.855	6	2	0	3.8878	3.8975	0.0097	2.9	22.884	0.015
24.005	6	2	2	3.7069	3.7133	0.0064	92.8	24.017	0.006
25.085	4	4	4	3.5491	3.5558	0.0067	2.3	25.102	0.009
26.115	6	4	0	3.4098	3.4179	0.0081	24.3	26.145	0.015
27.120	6	4	2	3.2858	3.2935	0.0077	72.8	27.150	0.015
29.000	8	0	0	3.0736	3.0841	0.0105	3.5	29.065	0.032
29.950	8	2	0	2.9818	2.9884	0.0066	100.0	29.980	0.015
30.835	8	2	2	2.8978	2.9046	0.0068	15.2	30.871	0.018
32.540	8	4	0	2.7491	2.7562	0.0071	20.1	32.586	0.023
33.380	8	4	2	2.6828	2.6888	0.0060	7.2	33.414	0.017
34.180	6	6	4	2.6212	2.6276	0.0064	62.5	34.224	0.022
36.500	8	6	0	2.4589	2.4658	0.0069	6.2	36.560	0.030

TABLE-6
X-RAY DIFFRACTION DATA FOR FASBC-5

2θ	H	K	L	d-cal. Value	d-obs. Value	Δd value	Rel.Int. (%)	2θ cal.	Δθ
7.220	2	0	0	12.2922	12.2639	–0.0283	88.5	7.195	–0.013
16.135	4	2	0	5.4972	5.5023	0.0051	41.0	16.130	–0.002
17.680	4	2	2	5.0183	5.0248	0.0065	3.9	17.681	0.001
20.445	4	4	0	4.3459	4.3511	0.0052	11.1	20.444	0.000
22.870	6	2	0	3.8871	3.8949	0.0078	5.1	22.888	0.009
24.000	6	2	2	3.7062	3.7141	0.0079	93.2	24.021	0.011
26.105	6	4	0	3.4092	3.4192	0.0100	29.7	26.150	0.022
27.105	6	4	2	3.2852	3.2952	0.0100	85.3	27.155	0.025
29.045	8	0	0	3.0731	3.0794	0.0064	4.8	29.070	0.013
29.935	6	4	4	2.9813	2.9899	0.0086	100.0	29.985	0.025
30.830	6	6	0	2.8973	2.9051	0.0078	17.1	30.876	0.023
32.525	8	4	0	2.7486	2.7575	0.0089	21.3	32.591	0.033
33.365	8	4	2	2.6824	2.6899	0.0075	9.1	33.420	0.027
34.160	6	6	4	2.6207	2.6291	0.0084	63.8	34.230	0.035
35.770	8	4	4	2.5091	2.5144	0.0053	8.5	35.802	0.016
36.515	8	6	0	2.4584	2.4648	0.0064	10.0	36.567	0.026
39.465	8	6	4	2.2826	2.2871	0.0045	2.7	39.496	0.015

Type of crystal system = cubic; Lattice parameters: a = b = c = 24.58 Å; $\alpha = \beta = \gamma = 90°$; Volume of unit cell = 14850.65 Å.

TABLE-7
X-RAY DIFFRACTION DATA FOR DEGUSSA

2θ	H	K	L	d-cal. Value	d-obs. Value	Δd value	Rel.Int. (%)	2θ cal.	Δθ
7.205	2	0	0	12.2970	12.2894	–0.0076	73.9	7.192	–0.007
10.195	2	2	0	8.6953	8.6909	–0.0044	58.1	10.177	–0.009
12.500	2	2	2	7.0996	7.0930	–0.0066	47.1	12.473	–0.014
14.010	4	0	0	6.1485	6.3318	0.1833	0.6	14.412	0.201
16.130	4	2	0	5.4994	5.5040	0.0046	37.2	16.124	–0.003
17.635	4	2	2	5.0202	5.0376	0.0174	2.1	17.675	0.020
20.395	4	4	0	4.3476	4.3617	0.0141	11.2	20.436	0.021
21.690	4	4	2	4.0990	4.1041	0.0051	57.6	21.690	0.000
22.865	6	2	0	3.8886	3.8958	0.0072	5.4	22.879	0.007
23.995	6	2	2	3.7077	3.7148	0.0071	95.8	24.012	0.009
26.105	6	4	0	3.4106	3.4192	0.0086	25.9	26.139	0.017
27.095	6	4	2	3.2865	3.2964	0.0099	80.3	27.145	0.025
29.020	8	0	0	3.0742	3.0820	0.0078	2.9	29.059	0.019
29.940	6	4	4	2.9824	2.9894	0.0070	100.0	29.974	0.017
30.840	6	6	0	2.8984	2.9042	0.0058	13.8	30.864	0.012
32.530	8	4	0	2.7497	2.7570	0.0073	19.3	32.579	0.024
33.355	8	4	2	2.6834	2.6907	0.0073	5.9	33.406	0.026
34.160	6	6	4	2.6217	2.6291	0.0074	60.9	34.216	0.028
35.760	8	4	4	2.5101	2.5089	–0.0012	8.7	35.788	-0.014
36.505	8	6	0	2.4594	2.4593	–0.0001	7.7	36.552	0.023
37.305	8	6	2	2.4116	2.4084	–0.0032	1.3	37.302	–0.001
37.985	6	6	6	2.3665	2.3669	0.0004	5.9	38.040	0.027

Type of crystal system = cubic; Lattice parameters: a = b = c = 24.58 Å; $\alpha = \beta = \gamma = 90°$; Volume of unit cell = 14850.65 Å.

The lattice parameters of FASBC-1 to FASBC-5 are shown in Table-1. The value of lattice parameter for the sample FASBC-3 is the same as that reported for theoretical value and also matches very closely with the value obtained for standard zeolite-A. The lattice parameters of zeolite-A standard, *i.e.*, Degussa is almost similar to the theoretical value[11]. All other FAZ-A samples have lattice parameter values almost in the range of the standard and the theoretical value. The slight variations are of the order of 0.01–0.02 Å. These alterations are due to the small instrumental error in the 2θ scale and can be rectified by zero correction parameters. These results are indicative of synthesis of highly pure crystalline phase of zeolite-A from flyash.

The synthesised FAZ-A was compared with its commercial counterpart,

Degussa (Germany) for its efficiency of removing some heavy metals. The comparative removal of Pb(II), Cd(II) and Cu(II) is represnted in Fig. 7. The results obtained indicate that the FAZ-A has almost similar efficiency as that of Degussa[11].

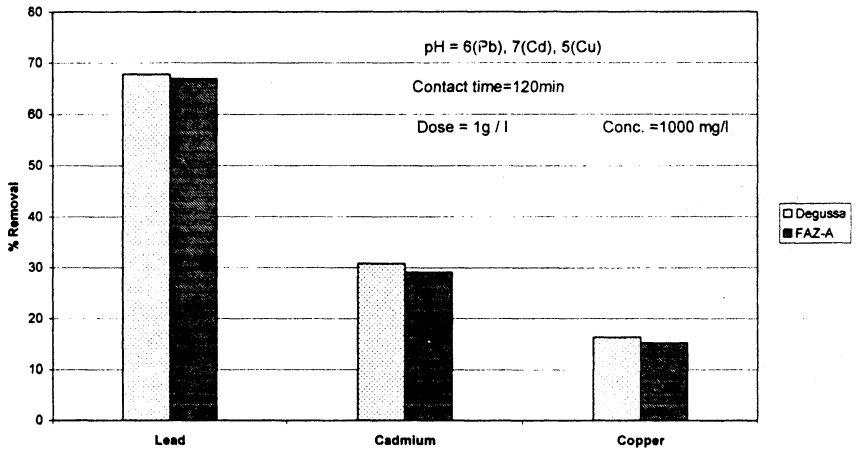

Fig. 7. Comparison of removal efficiency of FAZ-A with standard-A (Degussa)

Conclusion

Powder X-ray diffraction analysis of zeolite-A samples synthesized from flyash has well developed crystalline structure which is relatively pure, *i.e.*, the incorporation of other elements in the matrix is not significant. This conclusion is substantiated by the fact that the lattice parameters of FAZ-A closely match with those reported in literature and commercial Zeolite-A.

The purity of the as such synthesized sample is also substantiated by comparable results obtained for sorption of ammonia and heavy metals *vis-a-vis* commercial zeolite-A.

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