

Estimation of crystallinity in flyash-based zeolite-A using XRD and IR spectroscopy

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Various processes have been developed for synthesis of zeolite-A from flyash (FAZ-A), which have been patented nationally and internationally. The processes developed include five different methodologies with variations in pretreatment steps, sodium aluminate addition, etc. as a function of structure development and exchange capacity. Infrared (IR) spectroscopy has been used to study the framework structure of zeolites and also estimate their crystallinity. A systematic investigation of the framework structures have been carried out in the range of 400–4000 cm^{-1} . Investigations were based on the assignment of IR band to certain structural groups in the various zeolitic framework structures. The per cent crystallinity of FAZ-A samples has been ascertained by comparing the ratio of intensity of the peak at 560 and 480 cm^{-1} with the corresponding ratio for a standard sample. The per cent crystallinity of FAZ-A is calculated using standard procedure. Results of crystallinity obtained by IR and X-ray diffraction (XRD) methods are comparable and range between 85 and 100%. Investigation using IR is found to be good for estimating crystallinity and structure elucidation and is complementary to XRD.

Keywords: Crystallinity, exchange capacity, infrared spectroscopy, structure elucidation, zeolite-A.

ZEOLITE-A has been synthesized from flyash and detailed methodologies are discussed elsewhere¹. The development of crystallinity of zeolite sample is a crucial parameter for assessing successful completion of synthesis of zeolite-A from flyash.

X-ray diffraction (XRD) techniques have been used for identification and quantification of zeolite-A phase. Several reports are available on using XRD method for estimating crystallinity^{2–4}. Infrared (IR) spectroscopy is used to study the framework structure of zeolites. A schematic investigation of the framework structures of many synthetic zeolites has been carried out⁵ in the range of 200–1300 cm^{-1} . Investigations of these spectra were based on the assignment of the IR bands to certain structural groups in the various zeolite framework structures. In order to conduct this assignment, it is necessary to know the basic zeolite structures. Hence, this method of investigation is complementary to the X-ray structural analysis.

Shigemoto *et al.*⁶ synthesized zeolite Na-A and zeolite Na-X by fusing flyash with sodium hydroxide followed by hydrothermal reaction. These zeolites were characterized by IR, Si²⁹ and Al²⁷ MAS, NMR, XPS/AES, etc.

This communication addresses comparative study of XRD and IR techniques for estimation of crystallinity in zeolite-A synthesized from flyash.

Flyash sample was collected from hopper of electrostatic precipitator of Koradi Thermal Power Station, Nagpur. All reagents used were of analytical grade, having 99.9% purity. Commercial zeolite-A was procured from Wako, Japan.

The flyash-based zeolite (FAZ) sample was synthesized by fusing flyash with sodium hydroxide. A homogenous fusion mixture was prepared by proper grinding and mixing of flyash and caustic soda in 1:1.2 ratio. This mixture was heated to 550–600°C for 1–1.5 h. The resultant fused mass was cooled, milled and mixed thoroughly in distilled water with simultaneous addition of sodium aluminate. The slurry was then subjected to aging for 8–10 h. This amorphous aluminosilicate gel was then subjected to crystallization between 90 and 110°C for 2 h. The solid crystalline product was recovered by filtration and was washed thoroughly till the filtrate pH was 10–11 and dried at a temperature of 50–60°C. Variations in reaction conditions leading to zeolite samples with different crystallinities and calcium binding capacities, are detailed in Table 1.

Powder XRD analysis was employed to monitor zeolite-A formation process by CuK α radiation using X-ray diffractometer. The FAZ-A samples and zeolite-A standard were scanned for 2θ in the range 5 to 50°. The *d*-spacing values reported in the literature for zeolite-A (11.99, 8.58, 7.01, 4.07, 3.68, 3.39, 3.26, 2.73, 2.60) have been used as the basis for identification and quantification of crystalline phases.

Crystallinity has been estimated for the synthesized samples by taking the sum total of relative intensities of ten individual characteristic peaks (Table 2).

For example, in FASBC-4 (see Table 3),

$$\frac{\text{Sum total of relative intensities of FASBC-4}}{\text{Sum total of relative intensities of standard}} \times 100 \\ = \frac{627.9}{636.8} \times 100 = 98.6\%$$

The infrared spectra of FAZ-A samples were recorded on Shimadzu 8201PC using KBr technique in the wavelength range of 400 and 4000 cm^{-1} . The characteristics of IR bands associated with standard zeolite-A are given in Table 4.

The per cent crystallinity of FAZ-A samples is ascertained by comparing the ratio of intensity of the peak at 560 cm^{-1} to that of peak at 464 cm^{-1} , with the corresponding ratios for standard zeolite-A sample procured from Degussa (Germany), considered to be 100% crystalline. The basis of this method has already been discussed⁷.

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Table 1. Physico-chemical characteristics with respect to variation in experimental conditions

Sample	Pretreatment step	Sodium aluminate composition	Sodium aluminate (ml)	Seeding (g)	Crystallization time (h)	Crystallinity (%)	Calcium binding capacity (meq/100 g)
FASBC-1		SA-II (Na ₂ O: 50.3%, Al ₂ O ₃ : 39%)	20		3	72	440
FASBC-2		SA-II (Na ₂ O: 50.3%, Al ₂ O ₃ : 39%)	20	+ve	3	85	470
FASBC-3	Sieving by 170 μm	SA-II (Na ₂ O: 50.3%, Al ₂ O ₃ : 39%)	20	+ve	3	100	500
FASBC-4	Sieving by 53 μm	SA-II (Na ₂ O: 50.3%, Al ₂ O ₃ : 39%)	20	+ve	3.5	100	540
FASBC-5	Sieving by 53 μm Magnetic separation Ferric hydroxide removed from SA-II	SA-VI (Na ₂ O: 20.2%, Al ₂ O ₃ : 18.4%)	42	+ve	3.0	100	540
Degussa theoretical value						100	

Flyash and caustic soda ratio = 1 : 1.2; Fusion temperature = 600°C; Fusion time = 1.5 h; Mixing and aging time = 8 h.

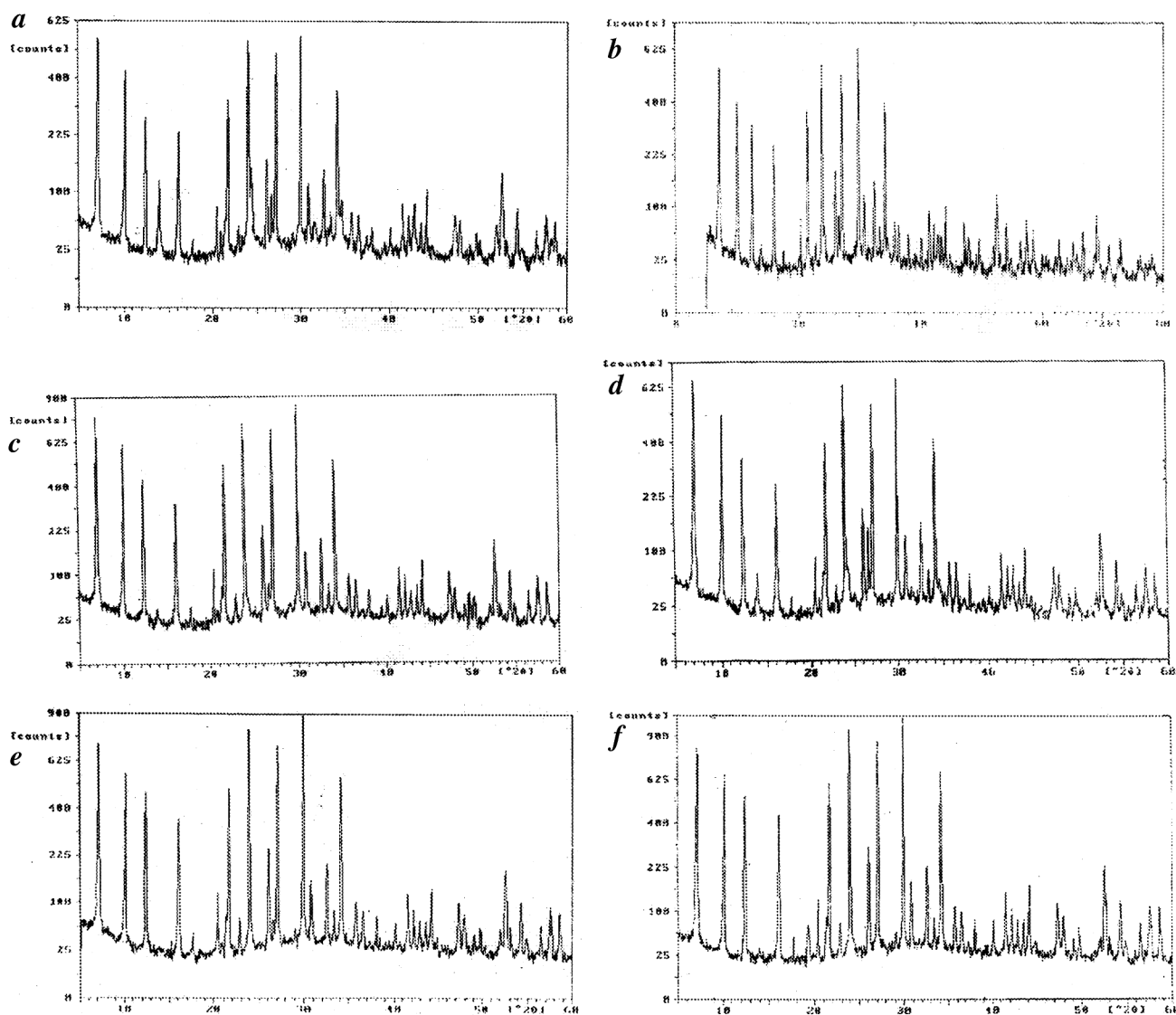


Figure 1. X-ray diffractogram of (a) FASBC-1, (b) FASBC-2, (c) FASBC-3, (d) FASBC-4, (e) FASBC-5 and (f) zeolite-A (standard sample-Degussa).

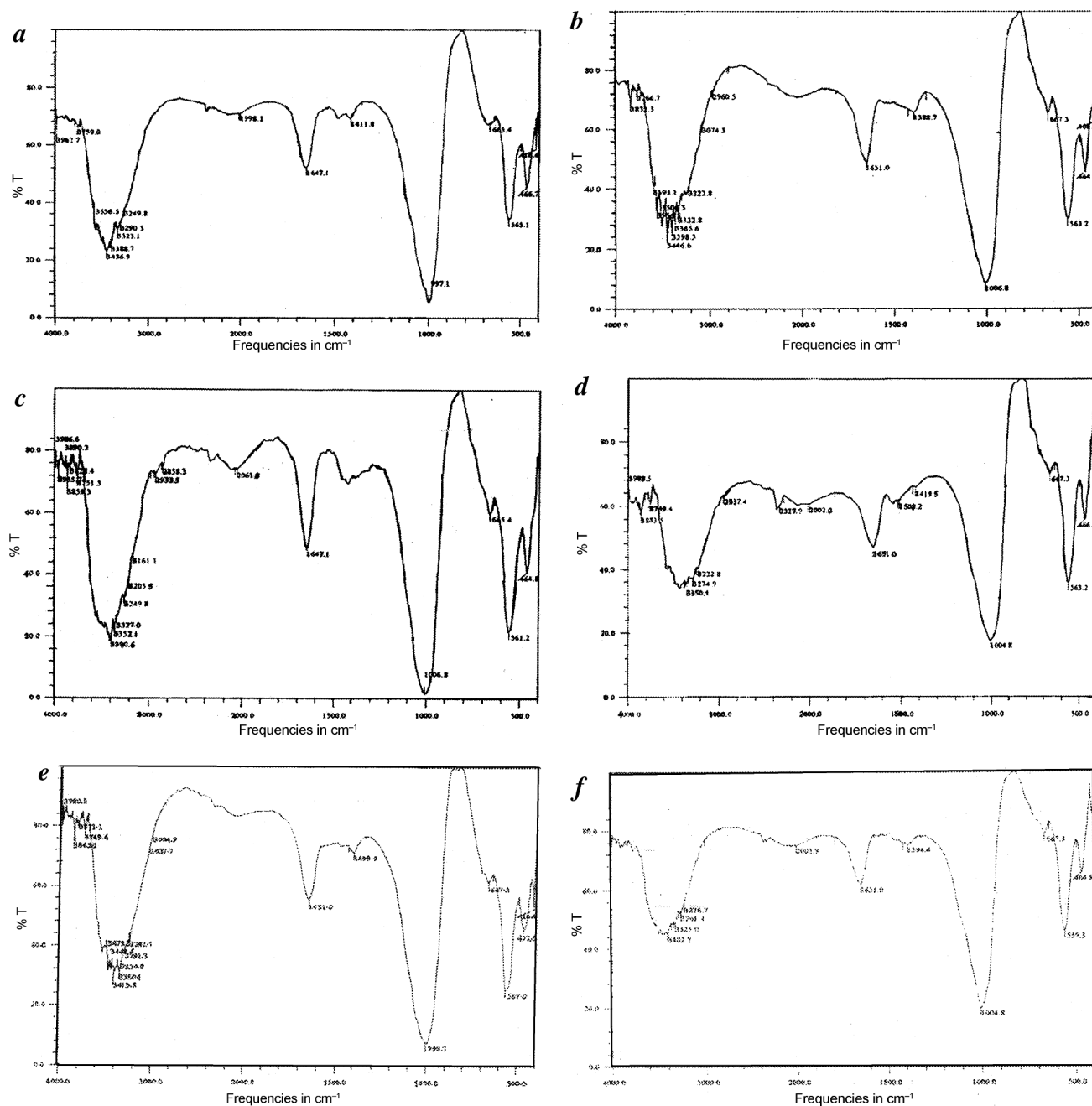


Figure 2. IR spectrum of (a) FASBC-1, (b) FASBC-2, (c) FASBC-3, (d) FASBC-4, (e) FASBC-5 and (f) standard zeolite-A (Degussa).

Table 2. Ten characteristic peaks and their relative intensities

Characteristic peak 2θ	Relative intensity for standard zeolite-A	Relative intensity for FASBC-4
29.950	100.0	100.0
24.010	95.8	93.0
7.210	73.9	81.8
27.130	80.3	76.8
10.205	58.1	62.2
34.165	60.9	61.6
21.680	57.6	56.1
12.490	47.1	50.9
16.130	37.2	37.2
26.095	25.9	28.1

The IR technique is proposed to be used for monitoring crystallinity during synthesis. There may be some impure phases associated with the zeolite-A phase being developed. These impure phases have negligible influence on its proposed application as an adsorbent/exchanger and have been accordingly used and reported elsewhere⁶.

The X-ray powder diffractograms of various FAZ-A samples, viz. FASBC-1, FASBC-2, FASBC-3, FASBC-4 and FASBC-5 and zeolite-A standard (procured from Degussa) have been recorded and shown in Figure 1 *a-f* respectively. The *d*-spacing values with respect to their intensities have been taken into consideration for estima-

Table 3. Per cent crystallinity of FAZ-A samples from FTIR and XRD

Sample	560 cm ⁻¹	Intensity A	464 cm ⁻¹	Intensity A	Ratio	Per cent crystallinity (from IR spectra)	Per cent crystallinity (from XRD)
	peaking intensity % T		peak intensity % T				
Degussa	45.891	0.3383	65.679	0.1826	1.85		
FASBC-1	34.225	0.4657	44.993	0.3468	1.34	72.4	72.8
FASBC-2	29.955	0.5235	45.780	0.3393	1.54	83.2	85
FASBC-3	21.723	0.6631	40.779	0.3896	1.70	92	98.6
FASBC-4	35.912	0.4448	56.056	0.2514	1.78	96.2	98.6
FASBC-5	25.254	0.5977	45.155	0.3453	1.73	93.3	98.6

Table 4. Characteristics of IR bands associated with zeolite-A

Type of IR band	Frequency (cm ⁻¹)
Asymmetric stretching of T–O* bond	1000–1500
Symmetric stretching of T–O* bond	660
Bending vibration of T–O* bond	464
D4R rings	560

T = Si or Al

Table 5. IR frequencies for different FAZ-A samples and standard zeolite-A

Sample	Frequency reported in literature (cm ⁻¹)					
	Peak-1 995	Peak-2 464	Peak-3 660	Peak-4 560	Peak-5 3400	Peak-6 1645
Degussa	1004.8	464.8	667.3	559.3	3402.2	1651
FASBC-1	997.1	466.7	665.4	565.1	3436.9	1647.1
FASBC-2	1006.8	464.8	667.3	563.2	3398.3	1651
FASBC-3	1006.8	469.8	665.4	561.2	3390.6	1647.1
FASBC-4	1004.8	466.7	667.3	563.2	3350.1	1651
FASBC-5	999.1	472.5	667.3	567.0	3413.8	1651

Table 6. Chemical composition and Si/Al of different FAZ-A

Sample	% SiO ₂	% Al ₂ O ₃	% Fe ₂ O ₃	% Na ₂ O	% H ₂ O	Si/Al ratio	SiO ₂ /Al ₂ O ₃ ratio
FASBC-1	33.20	28.50	1.33	14.70	19.0	1.03	1.96
FASBC-2	33.50	29.75	1.35	14.60	22.7	0.99	1.93
FASBC-3	34.10	28.50	1.07	15.00	21.5	1.05	2.03
FASBC-4	32.20	28.60	0.88	14.70	21.0	0.99	1.93
FASBC-5	30.32	27.70	0.80	14.60	22.6	0.97	1.85
Zeolite-A standard	32.20	28.50	0.02	14.00	22.0	0.99	1.93

tion of XRD crystallinity discussed earlier. The XRD crystallinity matches closely with that of commercial zeolite-A (Table 3). It is also comparable with crystallinity estimated using IR technique.

IR spectra for the five FAZ-A samples, namely FASBC-1, FASBC-2, FASBC-3, FASBC-4, FASBC-5 are given in Figure 2 *a–e*, respectively. The IR spectrum of FASBC-1 shows a sharp peak with high intensity at 997.1 cm⁻¹. This strong vibration is assigned to the Si–Al–O asymmetric stretching vibration. The sharp but less intense band at 466.7 cm⁻¹ can be assigned to the Si–Al–O bending mode. It is observed that the band recorded at 665.4 cm⁻¹, which

can be assigned to the Si–Al–O symmetric stretching has less intensity compared to the asymmetric stretching of Si–Al–O bond. This is likely as the probability of symmetric stretching of Si–Al–O bond is less compared to asymmetric stretching and bending. Another intense and sharp band occurs at 565.1 cm⁻¹, which is related to the presence of the double ring, D4R in the framework structure of FASBC-1.

FASBC-1 shows two IR bands, characteristic of the water of hydration of the zeolites. In zeolites, the water molecules are associated with cations and to some extent hydrogen bonded to the oxygen ions of the framework.

The broad band observed at 3436.9 cm^{-1} is characteristic of OH hydrogen bonded to the oxygen ions of the framework. In addition, an intense band at 1647.1 cm^{-1} , which is characteristic of the bending mode in the water molecule, is also observed. The sharp and deep band of FASBC-1 corresponding to the water of hydration, indicates higher percentage of water of hydration. IR frequencies observed for various samples are given in Table 5.

From Table 5 it can be seen that the other FAZ-A samples also show the characteristic IR bands, in the range discussed for FASBC-1. IR spectra of zeolite-A standard procured from Degussa (Figure 2f) shows the characteristic IR bands at frequencies similar to those of FAZ-A samples. It may thus be concluded that IR spectra of the FAZ-A samples and standard zeolite-A match quite closely, indicating presence of similar structural units and formation of identical chemical moieties in the FAZ-A samples. This is also in agreement with the results obtained from XRD studies.

Comparative evaluation of IR and XRD methodologies used for estimation of per cent crystallinity values shows that they match closely with each other for almost all the samples. Hence it may be concluded that the IR method can be used for monitoring crystallinity in zeolite samples being synthesized from a complex matrix like flyash.

Table 6 depicts the chemical composition of the samples. The desired purity level of zeolite phase is dependent on the end-application. Flyash-based zeolite material is presently being used as an adsorbent and ion exchanger, wherein the presence of trace-level impurities of metals like Fe and phase impurities like sodalite, etc. do not show significant detrimental effects.

IR method is successfully used for identifying zeolite structure as a complementary technique to XRD. The crystallinity estimated using IR and XRD methods is quite comparable and hence can be used as a method for monitoring the synthesis of zeolite-A from a complex matrix like flyash. Further studies are in progress for determining the sensitivity and accuracy of the method. The phase purity of the sample is important from the point of view of its usage as a catalyst. In case of environmental remediation, wherein it is to be used as an adsorbent/exchanger, purity of the sample is not a significant issue and can be compromised as a trade-off between cost and efficiency. Ultimately, the adsorbent medium is being used as a phase transfer for the pollutant and may either be disposed-off safely or converted into some value-added ceramic precursor, which may differ substantially in phase.

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Cold-tolerant fluorescent *Pseudomonas* isolates from Garhwal Himalayas as potential plant growth promoting and biocontrol agents in pea

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Four rhizospheric strains of *Pseudomonas fluorescens* (Pf), viz. Pf-102, Pf-103, Pf-110 and Pf-173 were antagonistic against *Fusarium solani* f. sp. *pisi* (causal agent of root rot in pea). In liquid culture assay, Pfs could inhibit the growth of *F. solani* f. sp. *pisi* by 60–100%, suggesting that their secondary metabolites were sufficient to antagonize the target pathogen. Mode of inhibition of *F. solani* f. sp. *pisi* by Pf-102 and Pf-103 was fungistatic, while Pf-110 and Pf-173 were lytic in their action. Plant growth promotion and *in vivo* antagonism assays against the target pathogen revealed that a consortium of four test strains was the best. Also individually, strains Pf-110 and Pf-173, capable of solubilizing inorganic phosphate and producing siderophore, were consistently better than the others. These activities are relevant to ecological fitness of the producer strains under the framework of organic farming underway in Uttaranchal.

Keywords: Biocontrol agents, Garhwal Himalayas, *Pseudomonas fluorescens*, pea, plant growth promotion.

SEVERAL microbes in recent times have been a focus of attention as plant growth promotion or biocontrol agents against

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