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Optimization of dry milling process for synthesizing nano zeolites

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Abstract

A series of experiments were carried out to optimize key parameters that are associated with dry milling process for synthesizing zeolites in the nano size regime. Milling time and rotational speed in planetary ball milling were the main parameters chosen for optimization. This study revealed that dry milling at 400 rpm for 5 hours resulted in 10-100 nm sized nanozeolites. Further, the morphology, stability and chemical nature of natural zeolite and milled zeolites were characterized using Particle Size Analyzer (PSA), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-Ray Spectroscopy (EDAX), Fourier Transform Infrared (FTIR) Spectroscopy and X-Ray Diffraction (XRD). Overall, the optimized milling process did not change the stability of zeolites, but on the other hand the changes in shape and crystallinity that are associated with top-down approach were observed and discussed in this paper.

Keywords: Ball milling, nanozeolites, stability, crystallinity

Introduction

Zeolites are naturally occurring crystalline aluminosilicates that are widely used as adsorbents, catalysts and ion-exchangers owing to their unique properties such as large surface area, defined pores and structures, high thermal and mechanical resistance with tunable chemical composition and most importantly recoverable and reusable (Chen *et al.*, 2012; Mintova *et al.*, 2013) [5, 11]. Such uniqueness of zeolite comes from its ordered three dimensional structures with microporous channels of interconnected tetrahedral, that is comprised of Al, Si and oxygen atoms. This crystalline structures is built from $(\text{AlO}_4)^{5-}$ and $(\text{SiO}_4)^{4-}$ bonded together. The general formula of zeolite is $\text{Me}_{2/n} \text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ (Bogdanov *et al.*, 2009) [2], in which Me refers to any alkaline or alkali earth atom and n being the charge on that atom, x is the number of Si tetrahedron that usually vary from 2 to 10 and y is the number of water molecules varying from 2 to 7. Such physical and chemical characteristics make natural zeolites, a most preferred mineral for employing in several applications. Researchers now focus on further improving the potential of these minerals by converting it into nanoscale materials. In recent times, nanozeolites are being exploited in agricultural sector as carriers of plant nutrients for smart delivery of nutrients (Manikandan and Subramanian, 2014); Subramanian and Sharmila Rahale, 2012; Thirunavukkarasu and Subramanian, 2014) [10, 15, 16]. Besides, nanozeolites are expected to revolutionize the area of environmental remediation for its high adsorption capacities (Lee *et al.*, 2016) [9]. Thus, the demand for nanozeolites is increasing steadily and this necessitates to evolve strategies to synthesize nanoscale zeolite materials by eco-friendly approach. Several methods such as hydrothermal synthesis, dry gel conversion method, ionothermal method, microwave/sonication assisted methods are available to synthesize nanozeolites. However, ball milling method, a top-down approach is widely recognized as a simple and eco-friendly to generate nanoscale materials (Wakihara *et al.*, 2011; Ejhieh and Khorsandi, 2014) [17, 6]. With this background, a series of experiments were conducted to optimize the dry milling process for synthesizing nanozeolites besides characterizing this nanoparticle to understand the influence of this method on structure and stability.

Materials and methods

The natural zeolite taken for study was obtained from GM Chemicals, Ahmedabad. The zeolite type used in this experiment was Clinoptilolite that belongs to the heulandite group and this

microporous framework is labelled as HEU by the Structure Commission of the International Zeolite Association (IZA-SC). The ball milling was performed by utilizing the planetary ball milling (Make: FRITSCH, Germany, Model name: Pulverisette 7) available at the Department of Nano Science & Technology, TNAU, Coimbatore. Based on preliminary studies, the Ball to Powder ratio of 5.3: 1 was optimized for conducting the experiments. Totally, 8 zirconium balls weighing 8 g each with 3mm diameter were used in the milling process.

Laboratory experiments were conducted to optimize the milling parameters such as milling time and rotational/milling speed to obtain nano-sized zeolites. In the first set of experiments, three ranges (400 rpm, 500 rpm and 600 rpm) of milling speed were performed with varied milling time such as 2 hours (H2), 3 hours (H3), 4 hours (H4) and 5 hours (H5). For instance, two hour milling time comprises of 8 cycles with a duration of 15 minutes per cycle. A pause time of 5 minutes between each cycle were given to eliminate excess heat. Based on the outcome of these experiments (details discussed in results and discussion section), the milling speed was optimized as 400 rpm and the natural zeolite were subjected to various milling time. The samples collected at different point of time were characterized as detailed below.

Particle size and stability

Particle size was measured using Nano Particle Size Analyzer (Model: HORIBA-SZ-100) that works based on the principle of Dynamic Light Scattering. The particles in the solution moves in a Brownian Motion, where a beam of light is scattered by a group of particles and the scattering angle of light is inversely proportional to the particle size. For measurement, 0.5mg of the dried sample were taken, added with 10ml of distilled water and sonicated for 1 minute for even distribution. The data obtained were plotted using ORIGIN Ver.8.0. Then the measures of dispersion stability were measured using the same instrument, in which the zeta potential/electrostatic forces were measured between -200 mV to +200 mV.

Scanning Electron Microscope (SEM)

The surface morphology was studied using Scanning Electron Microscope (FEI, Quanta 250) that uses an 'electron beam' to produce the image of the object and magnification is obtained by 'electromagnetic fields' (Kliwer, 2009) [11]. 0.5mg of dried powder sample was dispersed in 10 ml of deionized water, sonicated for 10 minutes. A small drop of the suspension were mounted on the carbon tape and allowed to dry before imaging at 40000X magnification.

Transmission Electron Microscope (TEM)

The ultra-structural morphology of the samples were studied under Transmission Electron Microscope (FEI Technai Spirit). 0.5mg of sample was dispersed in 10ml of distilled water, homogenized and a drop of solution containing zeolite was transferred on to the copper grid using micropipette. Then, it was allowed to dry and placed in sample holder for imaging by following the protocol outlined in Kliwer (2009) [11].

Energy Dispersive X-Ray Spectroscopy (EDAX)

EDAX, an analytical technique for elemental analysis was used to study the chemical composition of a sample. It was done in conjunction with SEM. About 50-100 mg of the zeolite sample was dusted on the carbon tape, mounted in sample table and the readings were recorded.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed to identify the functional groups using Jasco Model: R- 3000-QE. It measures the infrared region of the electromagnetic radiation spectrum and provides information about the bonds between different elements that absorb light at different frequencies giving the IR spectrum graph of IR light absorbance by the material and its frequency on Y-axis.

X-Ray Diffraction (XRD)

To determine whether the phase of zeolite is amorphous or crystalline, powder X-Ray Diffraction was performed in Shimadzu, Model: XRD 600, using Cu K α radiation ($\lambda = 1.54\text{\AA}$), monochromator, 40Kv current with scan speed of 10000 deg/min and scan range between 5 – 80000 degree. The powder samples were placed on the sample holders and then subjected for analysis by scanning between 2 θ angle of 5-85.

Results and Discussion

Size distribution and morphology

The characteristics of zeolites obtained at various milling time with milling speed of 400 rpm are presented in the Table 1. In this study, the milling speed was optimized as 400 rpm since the outcome of preliminary experiments with milling speed of 600 rpm and 500 rpm revealed that the milled zeolites were not within the required stability range (data not shown). The milling time for 5 hours produced zeolites in the size regime of 10-100 nm. Our results are in line with Mukhtar *et al.* (2013) [13] who had reported that milling time is the key parameter to produce nano zeolite as it produces effect on particle size and surface morphology.

Table 1: Characteristics of zeolite sampled at various milling time

S. No	Zeolite sample	Particle size (nm)	Zeta potential (mV)	SEM (nm)	TEM (nm)
1.	H0 (Natural)	2000-3000	-34.3	1500-3000	1000-2500
2.	H2 (Milled for 2 hours)	350-500	-56.1	300-460	350-570
3.	H3 (Milled for 3 hours)	220-350	-52.6	200-380	200-380
4.	H4 (Milled for 4 hours)	141-196	-58.6	100 -170	100-210
5.	H5 (Milled for 5 hours)	40-115	-46.9	50-90	10-50

*Results are average of three replications

The particle size distribution of zeolite milled at 2 hours, 3 hours, 4 hours and 5 hours were presented in the Fig 1. The

distribution lies between 300-550, 200-400, 100-200 and 50-100nm, respectively.

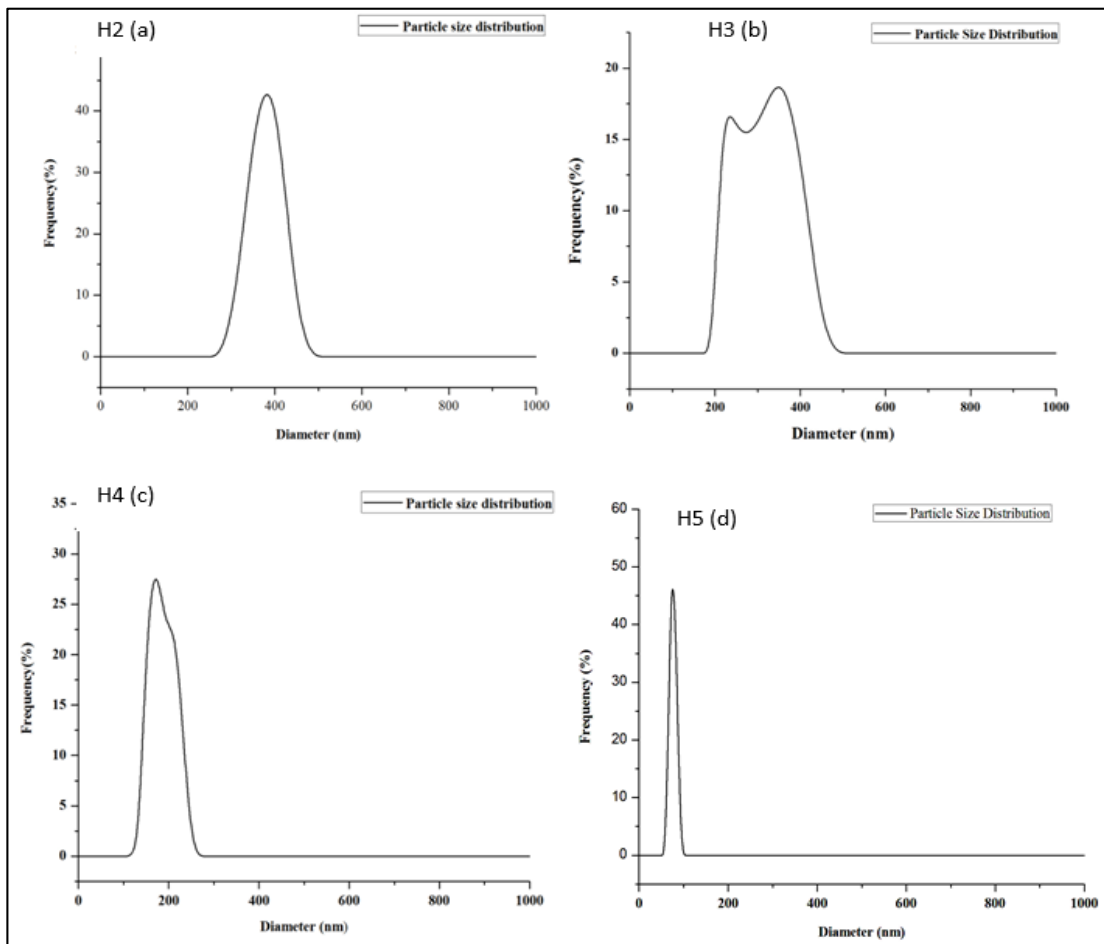
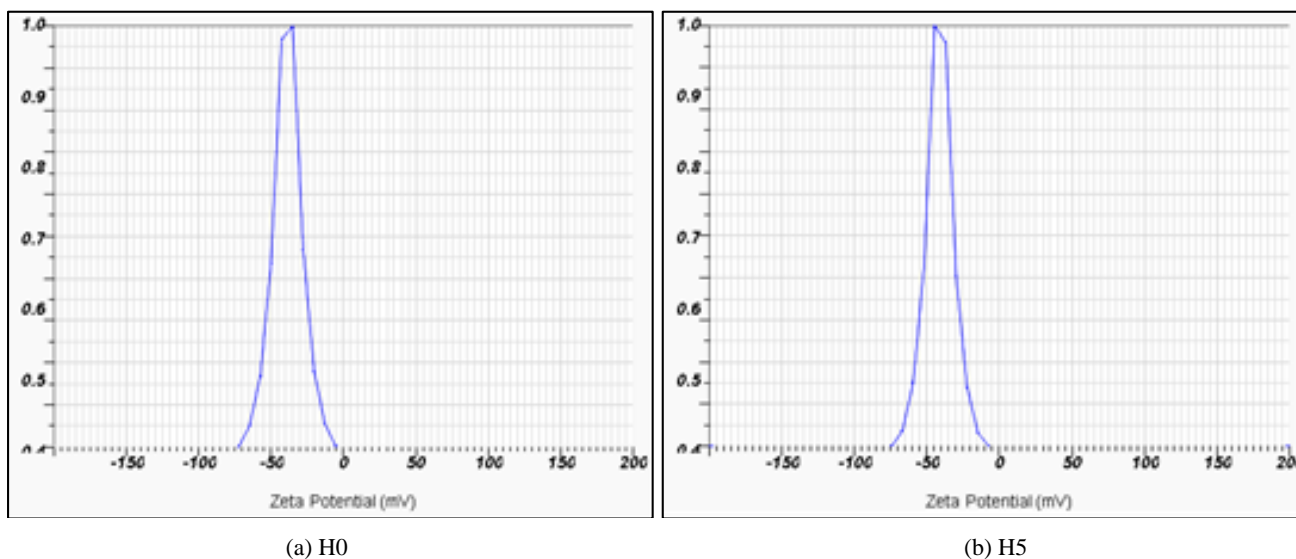


Fig 1: Particle size distribution of zeolites (a): milled for 2 hours (b): milled for 3 hours (c): milled for 4 hours and (d): milled for 5 hours

The zeta potential was measured between -30mV to -60mV proving that the stability of the particles in both cases (H0 and H5) were good and the negative sign of zeta potential showed that the surface of zeolite is negatively charged (Fig 2). This negative charge in zeolite is exhibited due to presence of excess oxygen in alumina molecules that is balanced by trapping positively charged ions in the cages. The size

measured by dynamic light scattering technique is not much reliable due to some limitation like multiple light scattering. In addition, the presence of even a smaller amount of large particle and closely spaced ones can compromise with the results. Thus, further confirmation of size was made in SEM and TEM.



(a) H0 (b) H5

Fig 2: Zeta potential of zeolite before (H0) and after ball milling (H5)

The natural zeolites (H0) were observed as cubical structures (Fig 5) and the milled zeolites in nano size range (after 5 hours) as spherical/oval in shape (Fig 3). These observations corroborates with the reports of Moshoeshoe *et al.* (2017) [12]

who observed that the initial cubic structure of zeolite was disturbed when subjected to ball milling and produced mostly spherical or oval shaped particles.

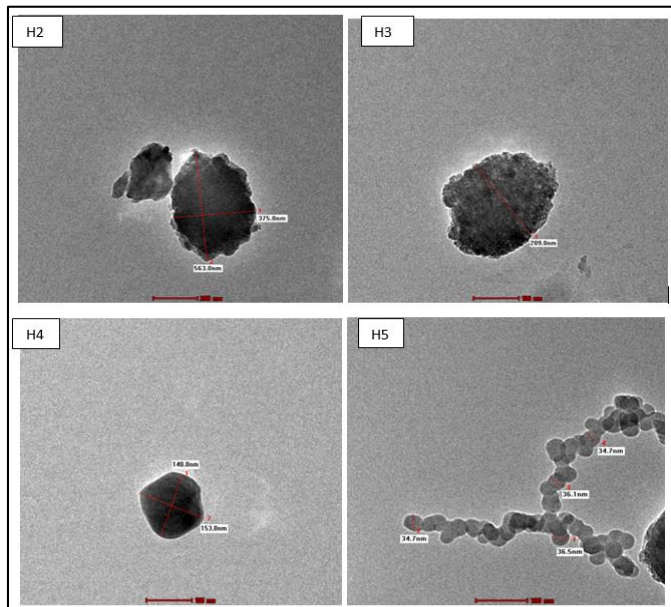


Fig 3: TEM image showing zeolite milled at different time duration

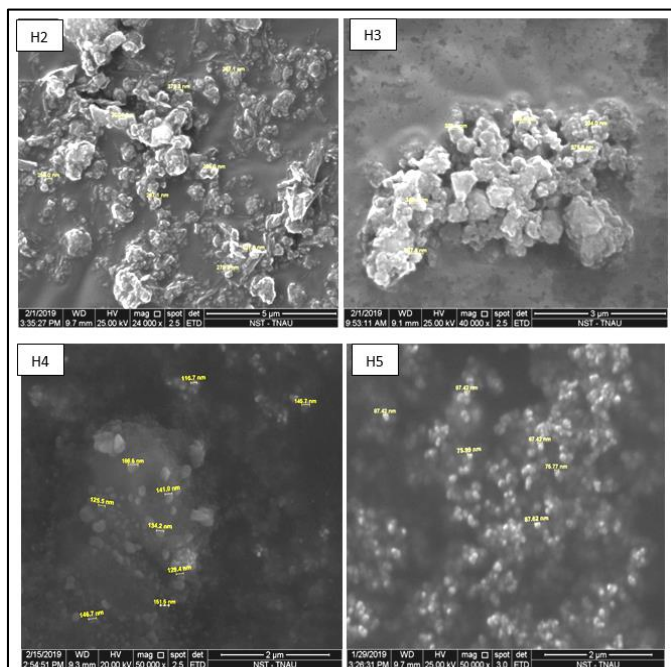


Fig 4: SEM image showing zeolite milled at different time duration

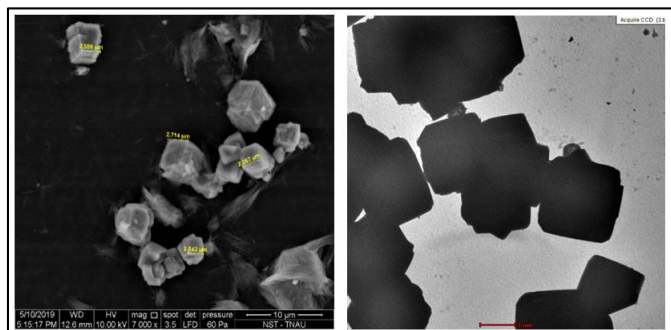


Fig 5: SEM and TEM image showing natural zeolite as cubic shaped

Chemical nature of the zeolites

The peak in EDAX observed shows the presence of Si with 32.24 weight percentage and Al with 07.77 weight percentage making the Si/Al ratio of 4.14 (Table 2). This observation is in line with the report of Moshoeshoe *et al.* (2017) [12] who

reported that the Si/Al in clinoptilolite zeolite ranges between 4.00 - 5.50.

Table 2: Chemical composition of natural zeolite estimated through EDAX

Element	Wt %	At %
C K	54.40	63.69
O K	36.10	31.73
SiK	32.24	21.12
Balk	07.77	00.92
NaK	03.20	01.45
MgK	02.70	01.56
CaK	02.80	00.98

As most of the natural materials exhibit in the active vibrational modes of Infrared, the FTIR was used as an ideal technique to analyze the functional properties of the zeolite before and after ball milling. The results of the FTIR measurements are shown in Table 3 and Fig 6. FTIR spectra of natural zeolite (H0) were compared with spectra exhibited by nanozeolite (H5). The band associated with symmetric vibrations of Si-O-Si and Al-O-Si is situated at 594 cm⁻¹ for natural zeolite and corresponding band in nanozeolite (H5) was observed at 610 cm⁻¹, indicating a slight frequency shift as a result of ball milling process. Similar peak shift in nanozeolite when compared to natural zeolites were also observed for the bands associated to asymmetric stretching vibration of [Si (Al-O)] and bending vibrations of HOH. The peaks observed at 728 cm⁻¹ corresponds to Na and 2360-2359 cm⁻¹ for CO₂ molecules that may be due to the impurities from atmosphere. Our observations corroborate with the earlier reports in zeolites indicating Na peaks at 728 cm⁻¹ (Ojuri *et al.*, 2016) [14], 1600-3700 cm⁻¹ to water molecules (Bohacs *et al.*, 2017) [3] and 2359-2365 cm⁻¹ to atmospheric CO₂. The band attributed to stretching vibrations of Mg⁺ was observed in natural zeolite at 3582 cm⁻¹. However, this was not observed in nanozeolite and it may be attributed to the milling process which might have affected the framework displacing these ions. Such observation is in line with the results of Bohacs *et al.* (2017) [3] who reported that the material structure of zeolite was changed due to mechanical activation. Thus, a slight frequency shift of FTIR peaks in the ball milled material when compared with the results of initial material were observed and it could be due to the effect of grinding.

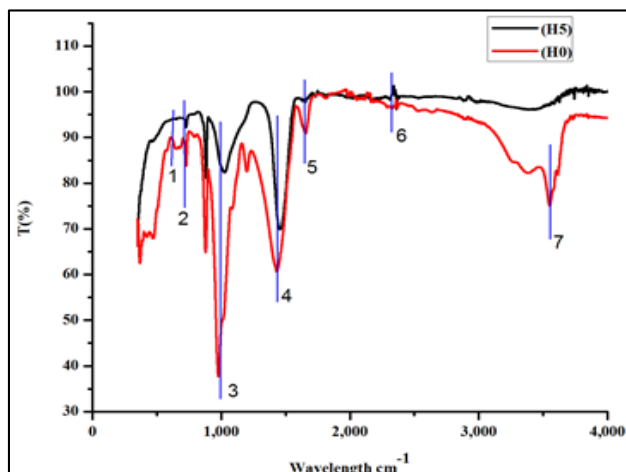
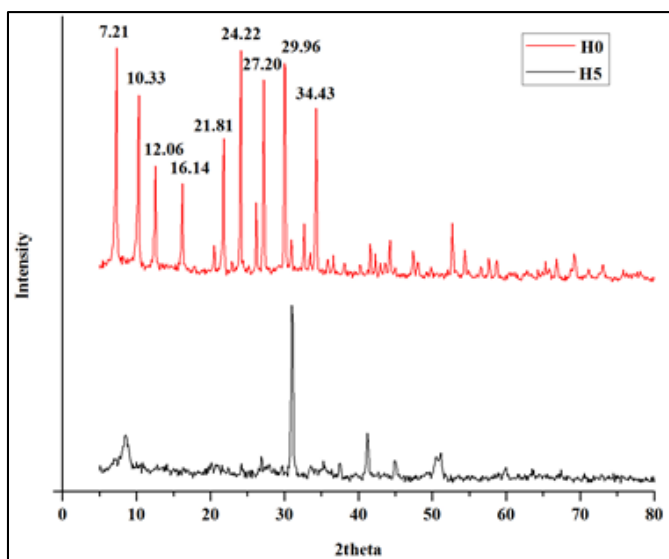


Fig 6: Comparing FTIR spectra for Natural zeolite before and after ball milling

Table 3: Peak wavenumber of bonds observed in FTIR spectra for natural (H0) and nanozeolite (H5)

No.	H0 (cm ⁻¹)	H5 (cm ⁻¹)	Corresponding band attributes
1.	594	601	Symmetric stretching vibration (Si-O-Si and Al-O-Si)
2.	728	728	
3.	1015	1021	Asymmetric stretching vibration [Si(Al-O)]
4.	1645	1648	Bending Vibration (HOH)
5.	2365	2359-2158	Atmospheric CO ₂
6.	3582 and 3551	-	Mg ⁺ and its associated water molecules

Patterns of XRD were obtained for all the samples and in the Fig 7, the patterns of natural zeolite and zeolite milled for 5 hours were compared. In the case of natural zeolite, nine prominent peaks at 7.21°, 10.33°, 12.06°, 16.14°, 21.81°, 24.22°, 27.20°, 29.96° and 34.43° were observed and the crystal system was recorded as cubic. Whereas in case of ball milled zeolite (H5), eight prominent peaks (as mentioned above) were not observed indicating that there is an intense reduction in crystalline nature of the zeolite after ball milling process. This may be attributed to the fact that grinding process may impose different forces upon particles, such as shear, attrition, compression, impact or internal forces thereby reducing the crystallinity (Kano and Saito, 1998) [7]. Furthermore, it is also reported that wet grinding causes shearing along the cleavage planes whereas dry grinding fractures the crystals (Akçay *et al.*, 2004) [1]. Hence, it is inferred that dry milling process causes amorphization of crystalline zeolites and this may be attributed to breaking of the structural Si-O-Si and Si-O-Al bonds and collapsing of the original crystal structure under the action of intensive mechanical forces (Charkhi *et al.*, 2010) [4].

**Fig 7:** XRD patterns of natural (H0) and nanozeolite (H5)

Conclusion

Nanozeolites were successfully synthesized by optimizing the dry ball milling process. This study has revealed that dry ball milling at 400 rpm for five hours was favourable to generate nanoscale zeolites (H5) with the size range of 50-100nm. Since the intention of optimizing the processing to synthesize nanozeolites for applying in agro-ecosystem, the ball milling approach was chosen as the process does not involve any chemical solvents and it is completely ecofriendly. Besides, the zeta potential measurements indicated that the produced nanozeolite was stable. Though FTIR results showed slight frequency shift, XRD pattern of nanozeolites recorded a reduction in crystallinity. Overall, this investigation has led to

the optimization of key parameters in dry milling process to achieve nanoscale zeolite. Since changes in shape and crystallinity in milled zeolites has been observed, further studies are essential to understand the effect of these materials on biological systems.

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