Ultrasonic Powered Hydrothermal Modification of Coal Fly Ash to Cost-Effective Zeolites

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Summary: Coal fly ash (CFA) waste is one of the anthropogenic materials having detrimental impact as particulate and leachate contaminant. Dumping of such solid waste into landfills and other improper waste management conduct can be lethal for environment. In this work CFA waste was attempted to modify into zeolites using ultrasonic assisted hydrothermal and conventional heating approaches. The conventional and ultrasonic assisted synthesized zeolites showed entirely different cation exchange capacity (CEC) and morphology. Overall, FTIR and XRD patterns of zeolites synthesized by both of techniques were almost similar. Overall, a better crystalline structure, functionality and morphology of Na-X, NaP1 and hydroxy sodalite (SOD) classes of zeolites synthesized in ultrasonic (USZ-8) and hydrothermal (HT-48) curing modes were observed. Hydrothermally treated (HT-8) material was found with a lower porosity and low CEC (109 meq/100g) in contrast to USZ-8 with high porosity and CEC (390 meq/100g) for the same reaction time. ICP-OES analysis demonstrated that ultrasonic cavitation was more appropriate way to convert coal fly ash based aluminosilicates into active zeolites, economically. It can be concluded reasonably that ultrasonic modification of coal fly ash into valuable zeolites is a constructive approach and a step to gear up greener innovation.

Keywords: Fly ash waste; Hydrothermal synthesis; Ultrasonic power; Zeolites.

Introduction

Coal is the worlds' most abundant, widely distributed and naturally occurring fossil fuel with ≈1000 billion tones global reserves [1]. It is considered as a fuel for vitality in numerous nations and its utilization in China and India has reached up to 79% and 69%, respectively [2]. However, the consumption of coal as a cheap source of energy in Pakistan is maximum about 50% [3]. Combustion of pulverized coal in power plants and boiler units produces fine particles that rise with the flue gases, called as fly ash. Coal fly ash (CFA) is collected from the exit point of a burner by using cyclones [4] or seized by dust collectors from the fume gases from the boilers of industries using coal as source of energy. Waste ash is a blend of about 80% fly ash and 20% bottom ash. CFA has negative impacts as a particulate ($\leq$ 75μm in diameter) and leachate pollutant for air and water bodies categorized as human carcinogen [5]. CFA is a solid waste comprises of inorganic oxides (COx, NOx, SOx), and poisonous chlorinated substances. Inhaling of carcinogens present in fly ash can cause lungs cancer and damage the immune system [6]. This solid waste contains number of leachable metals (Al, Fe, Pb, Cd, As, Sn, Ti, Sb) [7] which can disturb environmental cycles and poses serious threats to water and soil fertility. In addition, it tends to be responsible for brown haze (smog) and cloudiness bringing about exceptional air pollution [8]. Therefore, it is a wakeup call for the development of economical and environment friendly approaches to kick off such noxious solid waste in mass.

Due to the exponential consumption of coal as a cheaper source of energy, a massive amount of fly ash waste is being produced by different industries. Dumping of such a huge quantity of fly ash waste is an economical threat in addition to its environmental and health concerns [9]. To comprehend these ecological and practical issues different approaches are being implemented to utilize this waste to develop some value-added products and to generate revenue. Coal fly ash contains amorphous aluminosilicate glass which is a receptive stage for zeolite synthesis [10]. The synthesized zeolite adsorbents have efficient cation exchange capacity, which can be utilized for cleaning and softening of water by the removal of heavy metals and hazardous waste [11]. Zeolites are hydrated aluminosilicate materials which could be synthesized by the recycling of solid waste materials like CFA [12]. The general formula for a zeolite is $M_2O.Al_2O_3.xSiO_2.yH_2O$ in which "M" is alkali or alkaline earth metal, "x" ranges from two to ten and "y" changes from two to seven. Zeolites can be synthesized from variety of raw materials; however, in recent years many researchers paying attention to use CFA as a precursor [13]. The type of zeolite depends upon the experimental conditions and the ratio of fly ash to alkali along with temperature, pressure, heating

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technique and pH of the solution. Therefore, by adjusting the reaction parameters, diverse types of zeolites can be synthesized by using same fly ash as a raw material [14].

Ultrasonic (US) power can initiate reactions that may not be simple under conventional heating methods; furthermore, US irradiations accelerate the chemical reactions quickly [15]. Ultrasonic power causes cavitation events that refer to the growth and violent collapse of micro-bubbles in aqueous medium. The sonochemical effects of ultrasonic heating do not come from a direct interaction between ultrasonic field and molecular species, but it is due to acoustic cavitation [16]. The cavitation proceeds when gas nuclei present in the liquid go through oscillations, expansion and compression in ultrasonic field where vacuum is created into which gas diffuses in liquid. After multiple expansions and compressions, micro-bubbles reach a critical size resulting in bubble collapse and adiabatic heating occurred during that compression cycle. The cavitation creates radicals causing sonochemical reactions at the appointed time [17]. Elsewhere, it could enhance the dissolution processes and promote the chemical reactions, nucleation and crystallization kinetics [18]. All techniques viz; sonochemical, fusion or hydrothermal heating (HT), derive the combination of alumina and silica from CFA with alkali solution and finally precipitates into cost-effective coal fly ash-based zeolites (CFAZ) [19].

Experimental

Materials and sampling

Coal fly ash grab sample was collected as raw aluminosilicate source from electrostatic precipitator (ESP) of the boiler plant under the supervision of boiler engineer at Shabbir Textile Dyeing Industry, Faisalabad [20]. The striated sampled ash was stored in clean, airtight polyethylene bag and kept in a dark and desiccated place in the laboratory [21]. Sodium hydroxide (NaOH, 99% wt., Merck) of analytical grade was used.

Chemical composition and toxicity of coal fly ash

The chemical composition of the CFA sample was evaluated by X-rays fluorescence (XRF-PW-148- Philips) by standard method of characterization of advanced materials [22]. The leachate ability of the heavy metals from the CFA was examined by soaking in deionized water (DI-H_2O) for 48 hours at 25°C [23] by analyzing the concentrations of heavy metals with ICP-OES (Prodigy7-Teledyne Leeman Labs).

Physico-chemical properties of CFA and zeolites

First of all, CFA waste was pretreated for the synthesis of sodium zeolites. Fly ash sample was magnetically separated from iron particles and sieved under dry conditions by Tyler strainer of 80 mesh size to wipe out coarse materials leaving ash particles ranging from <150-200μm in diameter [24]. The moisture content of the subjected material was calculated by weighing in difference using drying oven in the laboratory following the standard protocols [25]. The specific gravity of the coal fly ash (CFA) and coal fly ash based zeolites (CFAZ) was determined by ultra-pycnometer [26]. Loss on ignition (LOI) was calculated by standard procedure [27] to check the un-burnt carbon content in CFA. Sorption behavior of raw CFA and synthesized zeolite (CFAZ) was determined by measuring the CEC in SI units as meq/100g of sample following the ammonium acetate method by ICARDA manual [28].

Conventional hydrothermal synthesis of zeolites

CFA zeolites were synthesized using hydrothermal treatment with NaOH activation at ambient temperature following the methods as reported in different studies [29]. Briefly, 25g of the precursor CFA (Si/Al > 2) was added to 250 cm^3 mineralizing solution (2M NaOH in DI-H_2O, pH = 12-13) at the solid to liquid ratio 1/10, for hydro gel formation. In the process of crystallization, hydrothermal reaction was carried out under dynamic reflux conditions at 120°C (maintaining the temperature of reaction mixture at 100°C) under atmospheric pressure (≈5 atm) in borosilicate flask [13]. Three samples of zeolite were prepared using 8, 24 and 48 h under individual reflux time with constant stirring. After washing and neutralizing, the residual gel was dried at ≈ 80°C for 8 h in electric oven [30]. Conventional hydrothermal (HT) conversion of CFA into value added active zeolites is presented in Fig 1.

Ultrasonic powered hydrothermal synthesis

In ultrasonic powered hydrothermal (USHT) synthesis, again 25g of CFA was added to 250 cm^3 mineralizing solution (2M NaOH in DI-H_2O) at solid to liquid ratio 1/10 for hydro gel formation. The crystallization reaction initiated by pouring the hydro gel into borosilicate double neck reaction flask under sono-thermal reflux heating ≈ 80 °C for 1 h using ultrasonic processor (DSA-SK1) facing autogenous pressure [29]. The sonicator produces acoustic waves of 40 KHz frequency consuming power of 100W by applying 220V.

In ultrasonic irradiations, the temperature of solution was raised to a steady state of ≈80°C within 5

min as ultrasonic energy operated directly into heterogeneous mixture [30]. The temperature of the reaction mixture was maintained at 80°C (±2°C) using water bath. Then the above mixture was subjected to hydrothermal reflux conditions at ≈100°C for 6 h under autogenous pressure. Finally, the mixture was again subjected to ultrasonic irradiations for 1 h and then the residues were separated and dried for further analysis. The process of ultrasonic powered modification of CFA to zeolite has been illustrated in Fig 2.
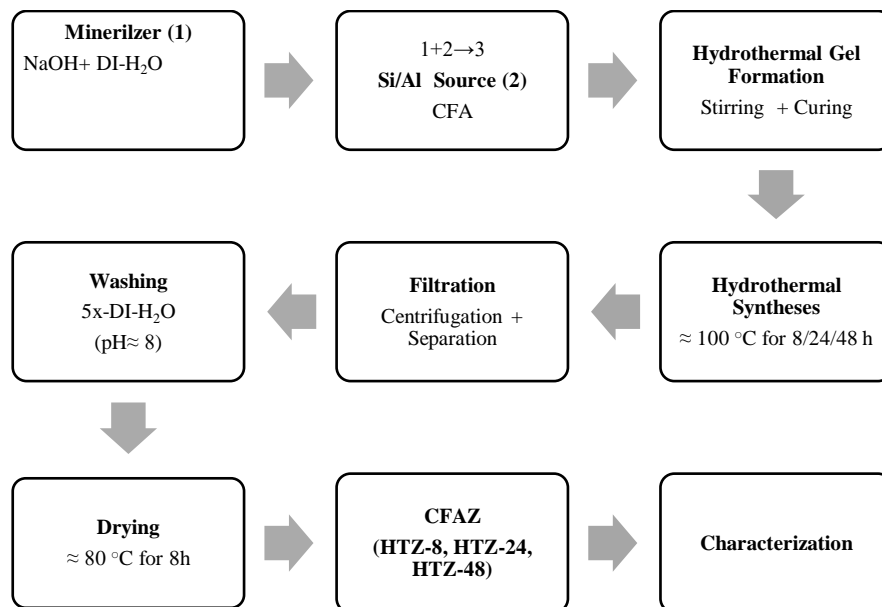
Fig. 1: Conventional hydrothermal (HT) modification of CFA into zeolites.
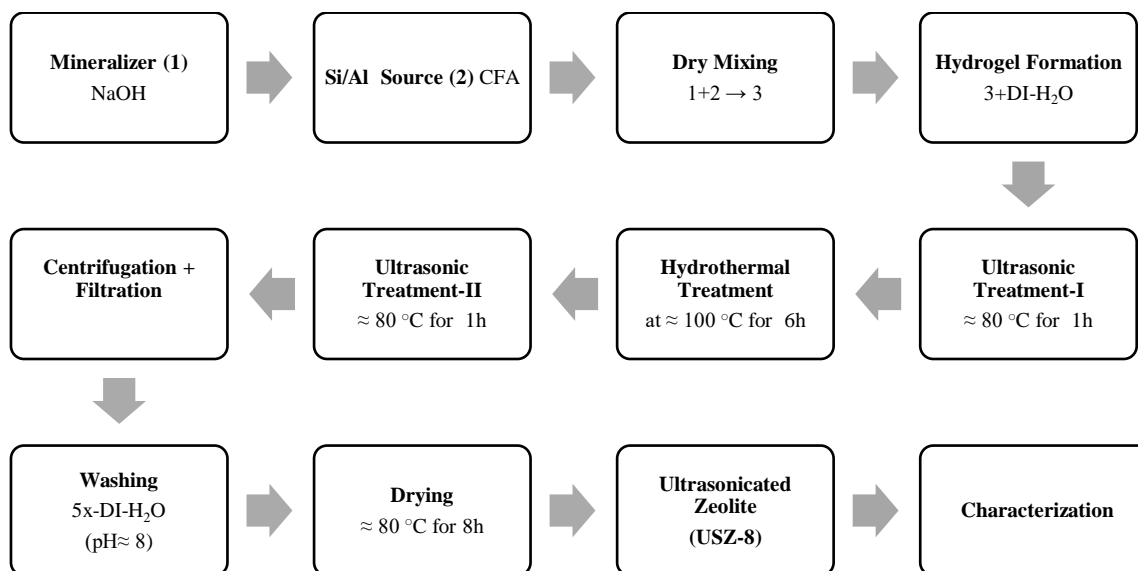
Fig. 2: Ultrasonic powered hydrothermal (USHT) modification of CFA into zeolite

Physico-chemical properties of supernatants of CFA and CFAZ

CFA waste (0.5 g) was dissolved in 10 mL of deionized water and shaken for 24 h at $30°C$ using orbital shaker and after trembling and filtration, the pH of the solution was determined by digital pH meter and electrical conductivity by multimeter water quality analyzer HI-9811-5 [22, 31]. Similarly, the pH and electrical conductivity of zeolites (CFAZ) supernatant was also measured. For elemental analysis, the microwave digested extract (MWDE) of CFA and zeolite supernatants obtained after the ultrasonic and hydrothermal processes were centrifuged at 2000 rpm. Then after decantation and filtration, the supernatants were diluted (0.005%V/V) and subjected to elemental analysis by ICP-OES (Prodigy-7 by Teledyne Leeman Labs), individually [32].

Characterization of CFA and CFAZ

The surface morphology of CFA and coal fly ash based zeolites (CFAZ) were investigated by SEM (JSM-5910 Scanning Electron Microscope, JEOL) under EHT= 15.00 kV, Signal A= SE1, WD= 8.0 mm, set of analytical conditions [33]. The crystallinity and mineralogical composition of CFA and CFAZ were identified by XRD analysis (Bruker D8 Advance X-ray powder diffractometer) by subjecting to Cu-Kα radiations and XRD data collection was conceded via 2θ in the range of 10-50°, with a scanning step of 0.02° [34]. The surface chemistry and functionality of CFA and CFAZ were investigated by FT-IR spectroscopy (Spectrum-2, FTIR spectrophotometer, Perkin Elmer) in the range of 3500-450 cm^{-1} in transmission mode [35-36].

Results and Discussion

Chemical composition and toxicity of CFA

The chemical composition and leaching behavior of CFA used for zeolite synthesis has been presented in Table-1. According to our present finding CFA was found to contain SiO_2 (63%) and Al_2O_3 (21%) as major constituents in addition to presence of minor contents of calcium oxide, titanium oxide and iron oxide. The leaching concentration of toxic heavy metals like As, Al and Ti from CFA was 0.085ppm, 34 ppm and 0.28 ppm, respectively. No doubt, in chemical analysis of different aluminosilicate sources like CFA, the combination of Al, Si, Fe and Ca may fluctuate locally and specific zeolites can be tailored by altering the adequate proportion of insufficient constituents. Si/Al ratio 3 (63/21) of investigated CFA

in the present study is quite fair for the synthesis of zeolites. So this CFA material can be used confidently for zeolite formation and residual metal and natural poisons can be managed without sufferings. Whereas, in any case, under acidic environment and long term storage and improper landfills of this massive solid waste can be wellspring for the contamination of ground water. Generally, CFA waste can be characterized into two categories, class "F" with CaO content less than 20% (Combustion by-product of high quality coal) and "C" with CaO content more than 20% (Combustion by-product of low quality coal) [37].

Keeping in view the compositional attributes of invested CFA, it can be categorized as "F" class ash. Raw fly ash comprises of Al_2O_3, SiO_2, F_2O_3 and CaO in the form of quarts, mullite, and hematite along with calcite minerals and inorganic compounds like lime (calcium carbonate) and gypsum (calcium sulphate) [38]. Commonly, low calcium fly ash contains quartz ($\geq$99% SiO_2), glass and mullite ($\geq$27% SiO_2 + $\geq$ 70 Al_2O_3) as the major constituents, while, high calcium fly ash includes high amount of mullite, calcium silicate, tricalcium silicate and tetra calcium aluminosilicate which are resilient to disintegrate in the synthesis even at high pH and retard crystal growth of zeolites [39]. It is obvious that, zeolites produced using CFA waste are not the same as amalgamations of such zeolites owes to less reactivity of Si and Al constituents and different cations (Fe, Ca) in raw materials which may frustrate the crystallization of zeolites [40]. It is insightful to examine the composition and leaching behavior of the virgin coal fly ash (CFA) during storage or before using of coal fly ash waste [41]. Actually, CFA displays a little dangerous impact due to heavy metals (Ti, As and Al) which can be diminished by suitable landfills to control the leaching of poisonous metals from ash that can reach at underground water bed [42]. Therefore, it is recommended that to cut the negative effect of coal burning or landfills in industrial units for an eco-friendly and greener transformation of industrial waste into valuable materials like zeolites [1].
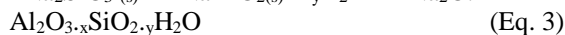
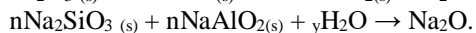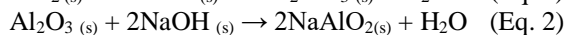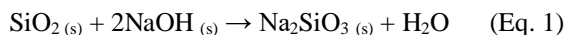*Ultrasonic power and mechanism of zeolite formation*

Recycling of industrial byproduct (CFA) into functional materials was the key target of this research. Here the valuable zeolites were synthesized by utilizing both existing and advanced techniques. CFA is a cheap and abundantly available material containing silica and alumina as vital constituent for the synthesis of zeolites [43, 44].

Table-1: Chemical analysis of CFA and its supernatants selected for ultrasonic powered synthesis of zeolites by XRF and ICP-OES

Metallic oxides	SiO₂	Al₂O₃	TiO₂	Fe₂O₃	Na₂O	K₂O	CaO	MgO	Others
Composition (% wt.)	63	21	1.5	2.8	1	0.8	1.8	0.6	7.5
Leached metals	Si	Al	Ti	Fe	Na	K	Ca	Mg	As
Concentration (ppm)	3.8	34	0.28	0.52	35	10	5.5	28	0.085

Ultrasonic powered synthesis allows a large amount of CFA particles to dissociate into the reaction mixture leading to higher yield of zeolites as USZ-8 (80%) as compare to HTZ-8 (68%) presented in Table-2. Sonochemical process results in elevation of heat up to 70-100 °C, within a short period about 5-10 minutes [45]. Fig. 3 shows a comparison between ultrasonic assisted heating and power output along with conventional heating which correspondingly speed up the reaction. Energy from ultrasonic power accelerates disintegration of aluminosilicate constituents and supports the bonds formation at the gel interface during CFAZ formation [30]. The bond formation speed up the buildup movement and hence accelerates the zeolite crystals arrangement. It is apparent that, ultrasonic condensation of 'Al' and 'Si' from any source either, pure precursors or from CFA waste reduces the crystallization time exponentially [46]. In present study it was observed that ultrasonic assisted heating act as an extra treatment in the form of blend process that alleviate the temperature sensibly. Well known crystalline stages were established in our present USHT treatment as compared to previous investigations where CFA with 1.9 ratio of Si/Al was treated under the similar set of conditions for 2 h and a noticeable zeolite formation was not observed [47].

According to mechanism of zeolitization, the constituents of CFA dissolve at a temperature range of 20-120 °C in initial step and the concentration of (OH⁻) in the basic solution makes a major involvement in zeolite crystallization. Disintegration and crystallization very much rely on the pH of reaction medium (Equations 1-3), where NaOH activator yields salt of Na-aluminosilicates [48]. The breakdown of insoluble minerals in the fly ash materials brings aluminosilicate into resulting gel that leads to fast conversion of CFA into active zeolite. Chemically, inactive ʠ-quartz and inert mullite crystallites react with NaOH agreeing to following empirical equations to yield active forms of silicates chiefly and aluminates scarcely.

$$SiO_{2\ (s)} + 2NaOH_{\ (s)} \rightarrow Na_2SiO_{3\ (s)} + H_2O \quad (Eq.\ 1)$$
$$Al_2O_{3\ (s)} + 2NaOH_{(s)} \rightarrow 2NaAlO_{2(s)} + H_2O \quad (Eq.\ 2)$$
$$nNa_2SiO_{3\ (s)} + nNaAlO_{2(s)} + {}_yH_2O \rightarrow Na_2O.$$
$$Al_2O_3._xSiO_2._yH_2O \quad (Eq.\ 3)$$

Where "n" is whole or fractional value while 'x' ranged from 2-10 generally ≥ 2, and "y" is the number of water molecules in the Na-zeolite and varies from 2-7 [49]. The Al₂O₃ and SiO₂ are the cationic framework responsible for tetrahedral crystalline system to tie together with oxygen atoms [50]. Overall, it is recognized that no twofold AlO₄⁻ are attached by sharing their corner in the framework of zeolite or it is established on the Lowenstein's standards. Al-O-Al linkages are not admissible where y/x is ≥1 [51]. The final products of alkaline hydrothermal treatment may shift between Zeolite-A (Na-A) [52], Zeolite-X (Na-X) [53], Philipsite (Na-P1) [54] and hydroxy sodalite (SOD) [13] under the applied set of condition of temperature, pressure, time, Si/Al ratio, pH and seeding process of the reaction used in the present study.
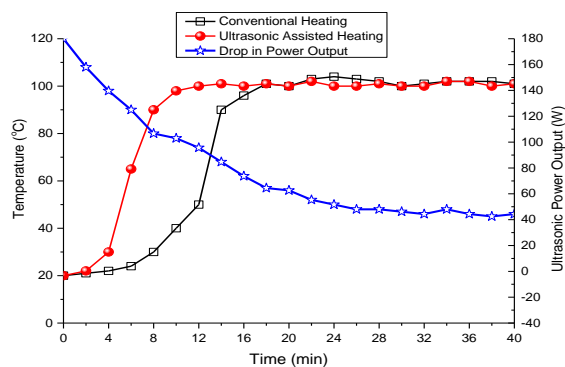

Fig. 3: Comparison of conventional and ultrasonic power output and temperature profile of reaction medium set against time for 2M NaOH solution.

Physicochemical characteristics of CFA and CFAZ

Loss on ignition (LOI) of studied CFA and CFAZ was identified as 3.5% and 0.2-1.2%, respectively. LOI value could be attributed to the presence of carbonates, water of crystallization and unburnt carbon. Encapsulated carbon in glassy crystallites is the most important constituent for LOI during incineration process. The specific gravity of CFA and CFAZ was observed 2.01 and 1.8-2.58 at 25 °C, respectively. Low specific gravity of raw CFA and hydrothermally synthesized zeolite (HTZ-8) shows the empty particles like cenospheres or plenosphere available as accumulation contrary to ultrasonic powered zeolite (USZ-8).

Table-2: Treatment and Physico-Chemical properties of CFA and CFAZ.

Sample	Treatment	LOI (%)	SG 25 °C	CEC meq/100g	Yield (%)
CFA	N/A	3.5	2.01	73	NA
HTS-8	HT 8h	1.2	2.58	109	68
HTS-24	HT 24h	1.1	2.65	215	70
HTS-48	HT 48h	0.8	2.57	212	75
USZ-8	US 2h + HT 6h	0.2	1.8	390	80

The specific gravity (SG) of fly ash covers a wide range, identical to the other physical parameters and usually ranges from a low 1.90 to high 2.96 for a sub-bituminous and iron-rich bituminous ash, respectively [55]. It was a noticeable consideration that the elemental composition, specific gravity and LOI of the water logged CFA remained unaffected as compared to virgin dry CFA. Table 2 demonstrates that no reaction is feasible even on simple hydration or wetting conditions unless we apply the basic condition for zeolitization [56].

CEC is the fundamental and significant property of zeolites which characterizes it for various modern applications. During the development process of dynamic zeolites, a portion of the tetravalent 'Si' atoms replaced by the trivalent 'Al' atom. This combination makes a shortage of a positive charge responsible for its cation exchange capacity (CEC). This charge is usually adjusted by the available little cations like Na^+ from NaOH that is directly connected to the proximity of active zeolite materials [22]. The findings of our present study showed that USZ-8 displays maximum CEC value (390 meq/100g) as compare to HTZ-8 (109 meq/100g) and raw CFA (73 meq/100g) signifying the worth of modern curing technique in zeolite synthesis. The synthesized zeolites (CFAZ) are permeable and mesoporous material with high CEC value encouraging to trap the target material (heavy metals) in its permeable voids. It was observed that CEC of the synthesized zeolites increases by increasing treatment time under the similar pH and temperature conditions in hydrothermal method. However, the advanced USHT synergized curing procedure keeps up high CEC in a least time span making it more cost-effective approach.

Physicochemical investigation of MWDE of CFA and supernatant of CFAZ

Supernatant of CFA showed slight basic pH (7.5) whereas the supernatants of CFAZ showed more basic pH (12.4-13.3). The high pH of CFAZ supernatants can be attributed to the addition of NaOH as mineralizer for the development of zeolites crystals. EC of deionized water used was very low and there was a non-significant increase in electrical conductivity of CFA extract (110 uS/cm) due to the presence of insoluble species in the mixture. But during the curing process the addition of NaOH as solid electrolyte, EC of CFAZ supernatants drastically increased at high temperature where the solvency favors thermodynamically. It was observed that ultrasonic cavitation further upgraded the dissolvability of aluminosilicate and raised the EC of USZ-8 (170 uS/cm) due to mineralizer and soluble ions in the reaction mixture. Electrical conductivity (EC) value is a quick, economical and reliable method of estimating the ionic substances present in solution [57].

Chemical analysis of stable oxide in residues and extract of the mixtures after the completion of Zeolitization process was carried out by ICP-OES that revealed percentage composition of elements. The concentration of Al (64-101ppm) and Na (240-1850ppm) was found impressively higher in the supernatants of CFAZ in contrast to microwave digested extract of raw CFA (Table-3). The high concentration of sodium (Na) can be attributed to the addition of NaOH in sonochemical and hydrothermal treatments. However, the chemical composition (Si, Al, Na) of ultrasonic assisted synthesized zeolite was radically different. Microwave-assisted digestion of CFA treatment not only shortens the sample preparation time but also requires less acid as compared to conventional wet digestion method [32]. In most of the previous studies demonstrate that the elemental composition (Si, Al and Fe) of zeolites and raw material is investigated from stable oxide phases [58]. Recent results also endorsed that CFAZ chemically composed of oxides of aluminum, silicon and sodium in hydrated form [59].

Table-3: Physicochemical properties of MWDE of CFA and Supernatant (0.005% v/v) of CFAZ.

Sample	EC (uS/cm)	pH	Si (ppm)	Al (ppm)	Na (ppm)
CFA	110	7.5	622	108	20
HTZ-8	124.6	12.5	4536	101.9	580
HTZ-24	167.8	12.4	5196	92	260
HTZ-48	154.2	13.3	11350	64	240
USZ-8	170	12.4	113500	85	1850

SEM micrographs of CFA and CFAZ

Scanning electron microscope (SEM) images of the CFAZ produced through conventional hydrothermal (HT) and USHT at constant temperature for variable reaction time are presented in Fig. 4. The micrographs of CFA and its CFAZ demonstrates the morphology and grain size of constituent minerals. Different magnifications (1µm=X10, 000, 5µm= X5,000 and 10µm= X1,000) were applied to identify the spherical and porous morphology of CFA and CFAZ, respectively. Zeolites from CFA after crystallization and filtration produces materials with variable morphology such as cubes for Na-X, needle like crystals for Na-P1 and flower shaped agglomerates reassembles to sodalite (SOD). Arrows in the micrographs representing spherical morphology of cenospheres especially in CFA micrographs. Squares covering mesoporous voids in the synthesized zeolites as mesoporous materials were observed as shown in USZ-8 image of x10,000 magnifications. The circles showing well-formed zeolite phases in different parts of CFAZ. The composition was characterized primarily by aluminosilicates as mullite and quartz phases, which occur in amorphous phase with different morphologies as prescribed in the previous studies [1]. The size and shape of crystals can be declared by interpreting the SEM micrographs of CFA and CFAZ [22].
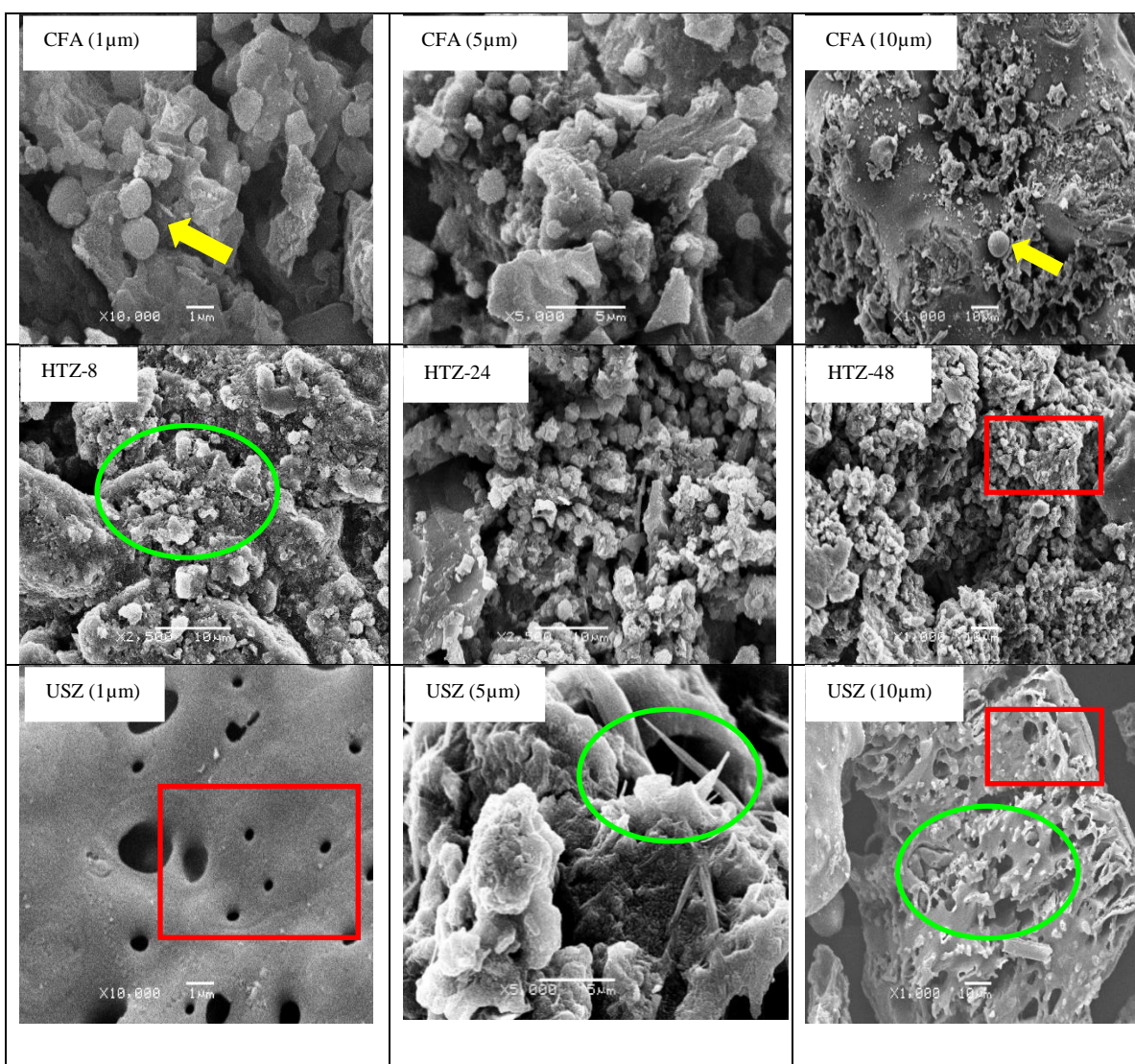

Fig. 4:   Micrographs of CFA and synthesized zeolites (CFAZ) via conventional HT and USHT techniques for various reaction time under variable magnifications.

XRD Analysis of CFA and CFAZ

The XRD results back up the success of both USHT and HT synthesis techniques in CFA conversion into active zeolites. XRD patterns showed the mineralogical composition dominated by the existence of amorphous (glass) as well as crystalline aluminosilicates (mullite "M" and quartz "Q") along with the presence of sodium silicate (Na_2SiO_3) and sodium aluminosilicate ($NaAlSiO_4$) as active zeolites. The presence of mineral phases of quartz (Q= ≥99% SiO_2), Mullite (M = ≥27% SiO_2 + ≥ 70 Al_2O_3), NaX (X)[$(Na_2)_{29}$ $(H_2O)_{240}(Al_{58}Si_{134}O_{384})$], NaP1(P) [$Al_2O_3$:10$SiO_2$:14$Na_2O$:840$H_2O$] and sodalite (S)[$Na_4$ Al $(OH)_3$ $(SiO_4)_3$] was confirmed by structure commission of international zeolite association and crystallography open database (COD) files [34].

Significant crystalline phases of zeolites were also developed under various treatment time using same alkali concentration as compare to CFA where only peaks of quartz and mullite present as silica and alumina mixtures (Fig. 5). Adjusting the same treatment time and alkali concentration, USHT was found superior to single mode HT activation technique for 8 h treatment time. Zeolite products in USZ-8 are comparable with HTZ-8 showing the high percentage of crystallinity of Na-zeolites (X, P, S) synthesized from CFA (Fig. 6). However, a comparison of two methods suggested the diverse mechanisms of controlling the synthesis of newly formed mineral phases [29]. X-rays diffraction (XRD) analysis had been a useful tool to check the presence of minerals viz., Mullite and Quartz as the main crystalline phases in CFA and its CFAZ [22].
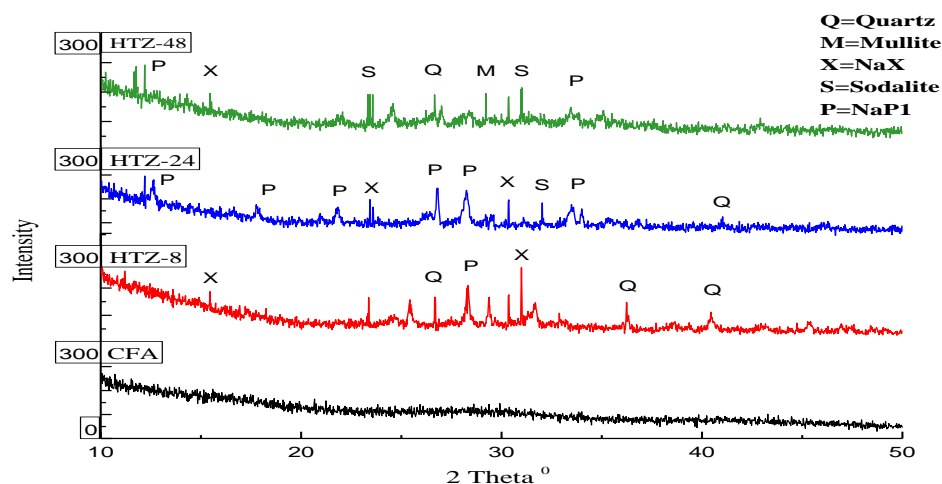

Fig. 5: Comparative XRD pattern of hydrothermally synthesized zeolite from CFA for variable reaction time.
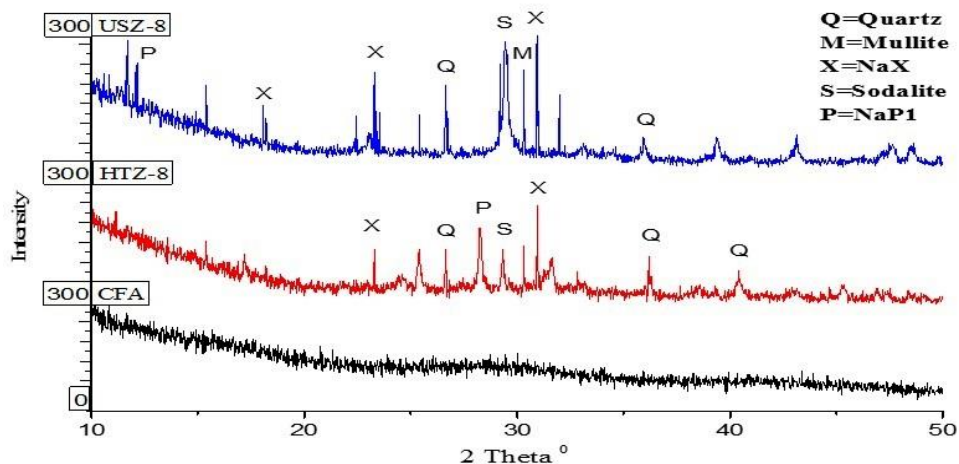

Fig. 6: Comparative XRD pattern of HT and UHST treated zeolites from CFA for 8 h reaction time.

FTIR spectra of CFA and CFAZ

FTIR spectrum of synthesized zeolites showed the asymmetric internal tetrahedral stretching vibrations ranged from 950-1250 cm^{-1} and symmetric stretching at 650-720 cm^{-1} of Si-O-Si and Al-O-Al. Similarly, Si-O-Si and Al-O-Al also showed the bending vibrations occurring at 420-500 cm^{-1} in CFAZ. The sharp peaks at 500-650 cm^{-1} only observed in USZ-8 represents the external linkages. Double ring systems and pore openings related vibrations that usually observed at below 420-300 cm^{-1} were not scanned in the given data of present study. Figure 8 showed that symmetric stretching for external linkages usually identified at 750-820 cm^{-1} were absent in FTIR spectra of our all samples whereas asymmetric stretching vibrations with sharp peaks at 1050-1150 cm^{-1} were only observed in USZ-8 sample [24]. The

appearance of bands at 1700–1600 cm^{-1} assigned to the presence of the H$_2$O molecules due to the (H-OH) vibrations in HTZ-24, HTZ-48 and USZ-8. The bands at 1570 cm^{-1} and 1412 cm^{-1} attributed to vibrations of the external hydroxyl groups in HTZ-48 synthesized for prolonged crystallization and hydrothermal curing [60].

Moreover, the observed single band at 3000-3400 cm^{-1} endorsed to the presence of hydroxyl groups in HTZ-24, HTZ-48 and USZ-8 [61]. FTIR spectra (Fig. 7 and Fig. 8) showed different Na-zeolites (NaP1, NaX and sodalite) phases in hydrated form developed from alumina and silica crystallites from CFA waste after USHT treatment with NaOH as activator.
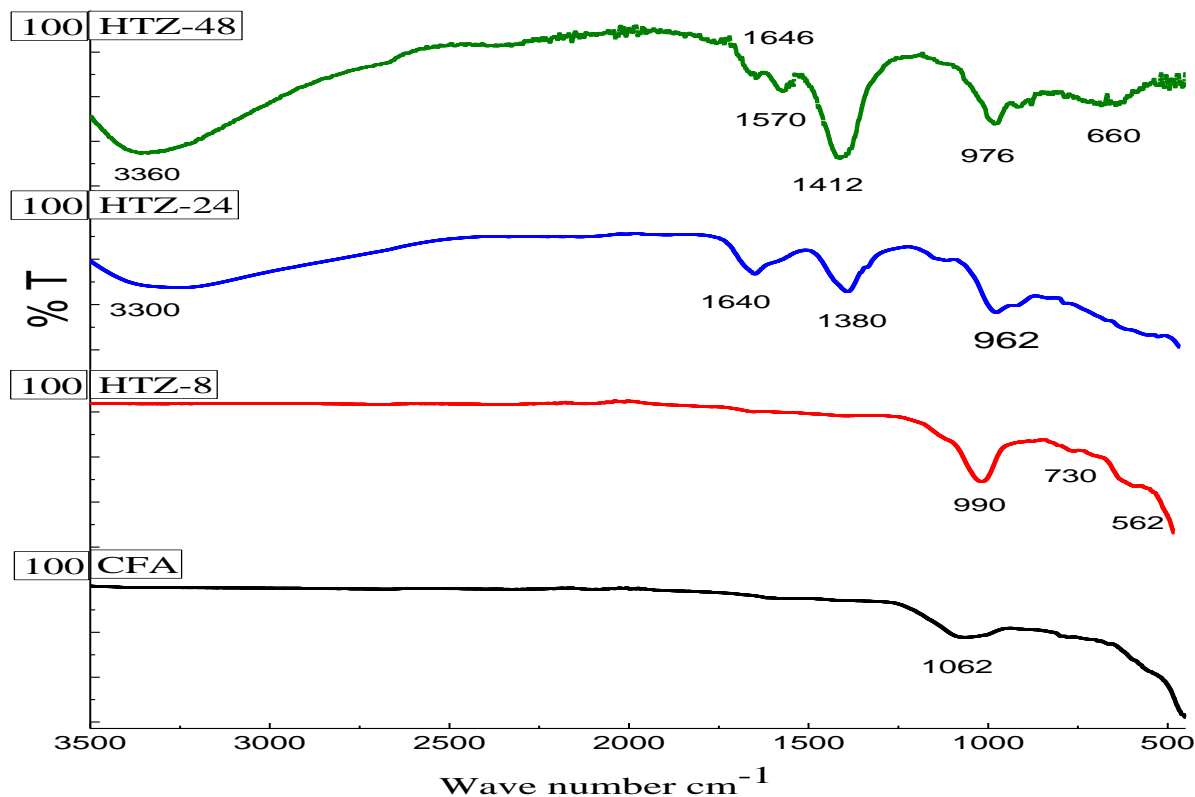

Fig. 7:   Comparative functionality of hydrothermally synthesized zeolite from CFA at various reaction time by FTIR spectroscopy.
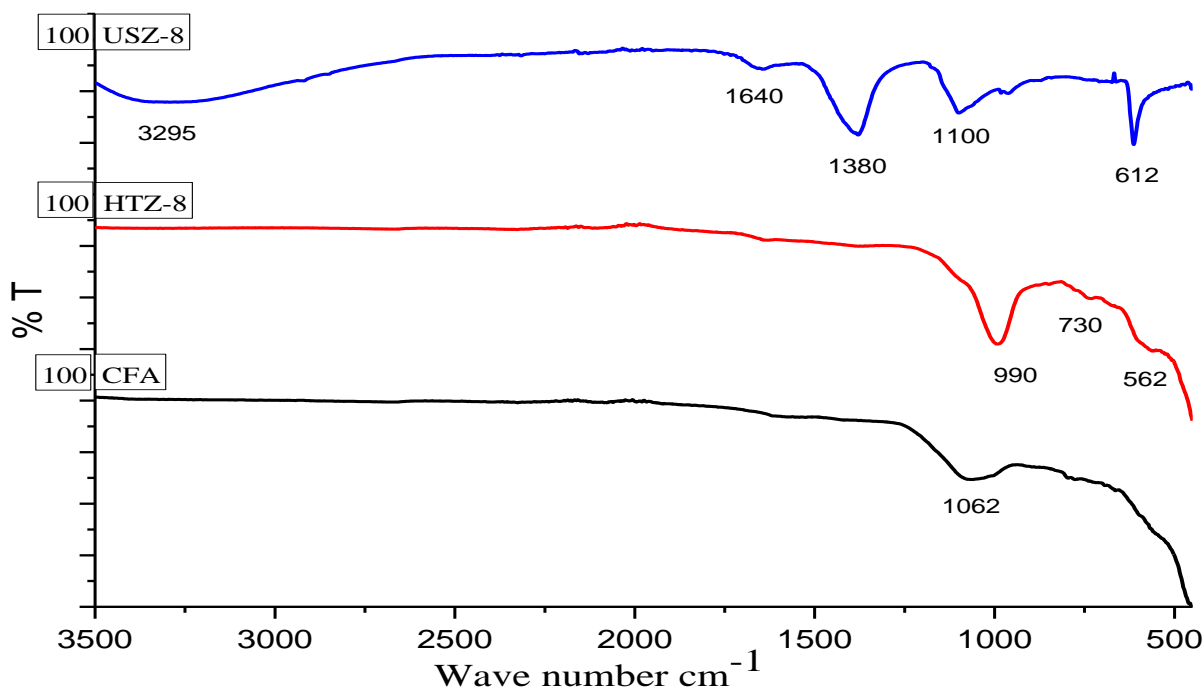
Fig. 8:   Comparative functionality of HT, UHST synthesized zeolite from CFA for 8 h reaction time by FTIR spectroscopy.

Conclusions

This study revealed that CFA as abundant industrial waste material could be a source of value addition materials (zeolites). Recycling of CFA through ultrasonic energy was found to be a most appropriate method to synthesize value added products like, NaX, NaP1 and Hydroxy sodalite types of zeolites. The sonochemical process not only improve the physico-chemical properties but also shorten the process time for the synthesis of zeolites. ICP-OES, XRD, FTIR and SEM are cutting edge characterization techniques to unfold the crystallization aspects of zeolites. Zeolite products showed the high percentage of crystallinity of Na-zeolites (X, P, S) synthesized from CFA. CEC is the fundamental and significant property of zeolites which characterizes it for various modern applications. High CEC of the developed products could find applications in different fields for the treatment and purification of waste water. Recent approach in utilizing "a waste to treat a waste" would be a promising remedy for sustainable society.

Acknowledgments

Conflict of Interests

None

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