

**Review Article**

**ZEOLITIC COMPOSITES FROM AGRICULTURAL DETRITUS FOR POLLUTION REMEDY: A REVIEW**

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**ABSTRACT**

An agricultural detritus bagasse fly ash (BFA) is a good source of silica and alumina which can be converted into zeolitic material by hydrothermal synthesis using conventional, microwave and fusion techniques. Zeolites derived from these techniques can also be modified by electrolytic media, surfactant, magnetite treatment and the ratio (Si/Al) adjustment to achieve enhanced properties for sorption study. Zeolite is an aluminosilicate compound with different structures and sizes. It has the best application in adsorption by the seizure of pollutants from the industrial effluent. It also has wide applications in catalytic activity in various syntheses. The bagasse fly ash and its derivatives are used for the removal of organic and inorganic contaminants in optimized conditions of adsorption such as pH, time, dose, concentration and temperature. Pollutants like phenols, dyes, pesticides, heavy metals and inorganic anions are successfully minimized from waste water using these bagasse fly ash zeolite composites.

**Keywords:** BFA, Zeolite, Synthesis, Pollution load, Review

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**INTRODUCTION**

Industrialization and globalization lead to the intense growth of pollution resulting in the addition of hazardous pollutants in the environment with the advancement in agrochemical, pharmaceutical, electroplating industries and dyes industries, accumulation of the pollutants in the environmental systems are various pesticides, organic intermediates, dyes and heavy metals, etc. These pollutants need to be monitored for human health safety. When the concentration of these pollutants crosses its permit limits, it needs remediation, which can be done by the extraction of the pollutants from the soils or aqueous systems or the reduction of their mobility and/or their in situ stabilization. There are several methods such as coagulation, flocculation, adsorption, solvent extraction and ion-exchange, etc. available as a treatment process. Adsorption is the simplest and most economical method useful for removal of pollutants from the environment. Adsorbents like silica gel, activated carbon, ion exchange resins, synthetic zeolites, bauxite, etc. have been used for this aim, but zeolite derived from bagasse fly ash and their modified forms give the advantages of low cost, availability in large quantities and having good mechanical, thermal properties [1].

The performance of different forms of zeolitic materials derived from bagasse fly ash has been studied for the treatment of waste water. The total worldwide production of sugarcane was approximately 1794 million tons in 2011 [2]. It is grown in different countries since the middle of the nineteenth century, for the production of sugar. It was only after the Global Energy crisis of 1973, that the scientists' and technologists' realized the value of sugarcane. Sugarcane is considered as one of the best converter of solar energy into biomass and sugar [3].

Biomass is an attractive source of activated carbon. Several studies have been reported showing the use of biomass and agroresidue as a source of porous materials. Among them, bugs have been explored for producing activated carbon by physical and chemical activation routes. Bagasse is normally used in the sugar industries as a fuel and resulting into bagasse fly ash as waste. The waste ash generated has a low amount of unburned carbon (20–33 wt %) and high amount of silica (60–67 wt %) The unburned carbon (bagasse fly ash carbon) has the potential to be separated and activated [4] by various activation methods to produce highly porous activated carbons prior to be used in the composite synthesis. Different activation methods will create different porosity and surface properties of activated

carbon. Silica is the main zeolitic precursors which can be extracted from fine bagasse fly ashes (BFA) particles using alkali digestion method. The type of zeolite composite product can be easily varied by controlling silica over alumina ratio in the reaction mixture [5].

In recent years, researchers have focused on another class of interesting recyclable adsorbents based on hydrophobic zeolites (high ratio of Si/Al) in the field of water treatment. The large adsorption capacities and stabilities are the major properties of zeolites which can be exploited for adsorption process. The influences of different physicochemical properties of zeolites are important for removal of various pollutants from the waste water [6]. For example, the adsorption capacity of phenol by HFAU zeolites was found to be in the range 0.6–0.7 mmol/g with an increase of Si/Al ratio from 5 to 500. Thus, a Si/Al ratio, as well as pore size, has the predominant effect on the adsorption capacity of phenol [7].

The aim of this review is to give a detailed account about methods of bagasse fly ash adaptation into the high value zeolitic material and its utilization as a pollution remedy.

**Zeolite**

Swedish mineralogist Cronstedt introduced "zeolite" in 1756 for certain silicate minerals in allusion to their behavior on heating in a borax bead (Greek *zeo*= boil; *lithos*= stone). Three minerals such as Stilbite, Analcime, and Harmotome were listed by Haüy (1801). Forty-six zeolites were listed by Gottardi and Galli (1985), and new species continue to be described in the present time. The first crystal structure determination of a zeolite was done by Taylor 1930 on Analcime; Hey (1930) concluded that zeolites have aluminosilicate frameworks with loosely bonded alkali or alkali earth cations or both. Molecules of H<sub>2</sub>O occupy extra-framework positions. It was pointed out that consequential requirements of the molar ratio are Al<sub>2</sub>O<sub>3</sub>: (Ca, Sr, Ba, Na<sub>2</sub>, K<sub>2</sub>) O = 1 and that of O: (Si+Al) = 2 in the empirical formula [8].

The crystalline aluminosilicates consist of Si and Al tetrahedral units (TO<sub>4/2</sub>, where T = Si or Al) which are linked through bridging oxygen atoms giving rise to secondary building units (SBUs). These units combine to generate frameworks with a regular distribution of molecular-sized pores and cavities. The general formula of zeolites is M<sub>x</sub>/n [(AlO<sub>2</sub>)<sub>x</sub> (SiO<sub>2</sub>)<sub>y</sub>]. zH<sub>2</sub>O, where M defines the compensating cation (usually from groups I or II) with valency n. The values of x, y and z depend on the type of zeolite [9].

The primary building unit for zeolites is the tetrahedron, and the secondary building unit (SBU) is the geometric arrangements of tetrahedra. The SBU is simple polyhedra such as cubes, hexagonal prisms, or cubo-octahedral. The structures can be formed by repeating SBUs and according to them; zeolites can be classified into eight groups. Chemical structure of zeolite is represented in fig. 1 while fig. 2 shows a primary building unit of zeolite structure [10].

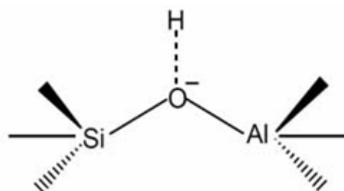


Fig. 1: Chemical structure of zeolite

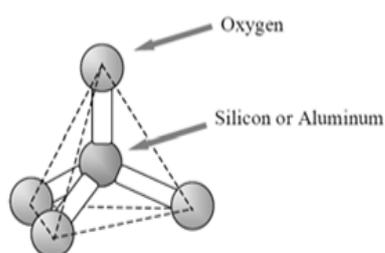


Fig. 2: Primary building unit of zeolite structure

Zeolite with an open structure framework consists of many channels and interconnected voids of discrete size (in the range 0.03-2 nm) which are occupied by cations and water molecules. Each  $AlO_4$  tetrahedron in the framework bears a net negative charge which is balanced by a cation. Which are mainly from IA and IIA groups of the periodic table. The cations can reversibly be exchanged for other ions possessing the same charge when aqueous solutions of ion are passed through channels and voids. This replacement results in the narrowing of the pore diameter of the zeolite channels. The water may be removed reversibly by the application of heat. The SBUs can be of simple arrangements of tetrahedra such as four, six, eight, ten or more complicated membered rings. Other factors such as the location, size and coordination of the extra-framework cations can also influence the pore size [10].

The sorption capacity and selectivity for water and other molecules are defined by zeolite porosity, pore size distribution, and specific surface [11]. Due to high affinity for water cation-containing zeolites are extensively used as desiccants. Hydrophobic silica based zeolites can preferentially adsorb organic moiety based on the different size, shape and polarity. A typical organic molecule entrapped in a pore channel is shown in fig. 3 [12].

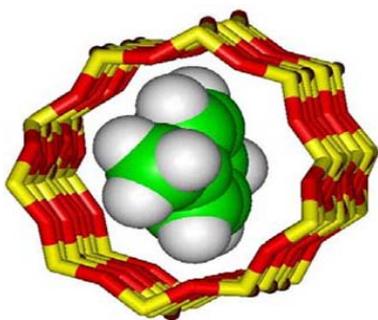


Fig. 3: A molecule in a channel Ion exchanger

Fig. 4 shows loosely bound metal ions in the extra framework of zeolite NaA type [12]. In aqueous media, they are readily exchanged with other metals. This behavior is observed in water softening alkali metals such as sodium or potassium of the zeolite are replaced by the calcium and magnesium ions from the hard water. Thus, many commercial washing powders contain zeolite. Industrial waste water containing heavy metals and radioisotopes in nuclear effluents may also be treated by zeolites for minimizing the environmental pollution.

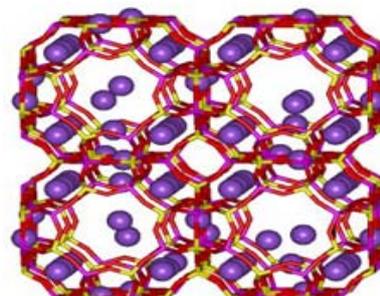


Fig. 4: Loose extra-framework metal ions

### Green catalyst

The current major challenges before chemists are to develop synthetic methods that are less polluting, i.e., to design clean or 'green' chemical transformations. Clays are widely used due to its non-toxic, non-corrosive, economical, recyclable and eco-friendly nature. Thus are efficiently used for a variety of organic reactions.

Montmorillonite (MMT) is one kind of monoclinic zeolite structure with formula  $Al_2Si_4O_{10}(OH)_2 \cdot nH_2O$ . It may appear in a variety of colors (e. g. Yellow-green, yellow-white, gray and white) due to other trace metal elements. It typically forms microscopic or very small micaceous crystals. Due to swelling affects, the volume of MMT crystal may increase several to thirty-fold after absorption of water. The crystalline structure of MMT consists of multiple layers and each layer made up of one octahedral alumina sheet sandwiched between two tetrahedral silica sheets.

They have been used as catalysts for a number of organic reactions and offer several advantages over classical acid catalysts. For example, the strong acidity, non-corrosive properties, cheapness, mild reaction conditions, higher yields, selectivity and the ease of setting can be easily explored advantages with the use of MMT. For instance, organic synthesis reaction fig. 5 shows pinacol coupling reaction [13].

### Pinacol coupling reaction

A pinacol coupling reaction is an organic reaction in which a carbon-carbon covalent bond is formed between the carbonyl groups of an aldehyde or a ketone in the presence of an electron donor in a free radical process. The reaction product is a vicinal diol. When the reaction of benzaldehyde and zinc chloride in aqueous THF under ultrasound is carried out by introducing Montmorillonite K-10 as a catalyst which reduced reaction time [13].

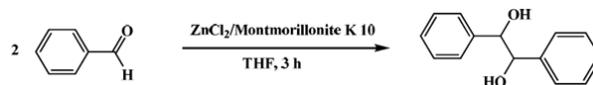


Fig. 5: Pinacol coupling reaction for the synthesis of vicinal diol

### Characteristics of bagasse fly ash

Sugar industry generates abundant of bagasse. The bagasse in boilers generates large quantities of fly ash. Assuming 25% bagasse in sugar cane, its generation is estimated to be more than 75 million

tons; burning of it would lead to the generation of around 3 million tons of fly ash annually i.e. 4% by weight of bagasse [14].

Hence, sugar industry faces the solid waste disposal problem of bagasse fly ash. Few parts of the BFA are utilized by cement and ceramic industries. The remaining unused part needs an appropriate utilization. Inappropriate dumping creates soil pollution and also causes air pollution with an allergic problem with human beings. Increasing concerns about the environmental consequences, such disposal has led to an investigation of other possible utilization avenues. BFA mainly contains aluminosilicates glass, mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), and quartz ( $\text{SiO}_2$ ) which are the required building blocks of zeolite formation. Furthermore, conversion of low-cost

byproduct into higher level zeolite would make the environmentally friendly disposal of BFA for more economical viable [15].

The thermal characteristic of BFA and its derived zeolites also was studied by Bhavna Shah *et al.* 2011. The thermogravimetric analysis curves (TGA and DTG) of bagasse fly ash (BFA) and synthesized CZBFA under oxidizing atmosphere are shown in fig. 6.1, fig. 6.2 under air atmosphere. Weight loss during the thermal analysis of the materials in the temperature range of 100 °C–800 °C are probably because of the removal of moisture, light volatiles or the evolution of  $\text{CO}_2$  and CO in both the native BFA and synthesized zeolite CZBFA. In BFA, the residue left is 79% ash at 850 °C whereas in CZBFA it is 74.83%.

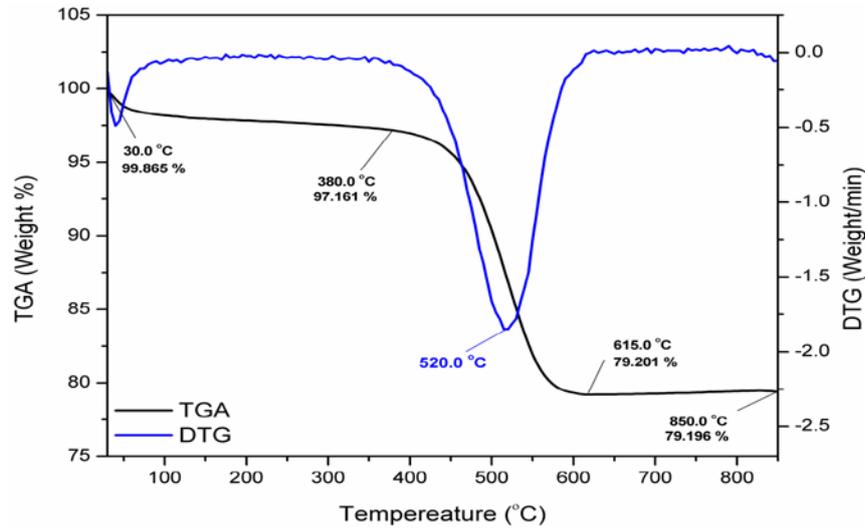


Fig. 6.1: TGA and DTG curves of BFA

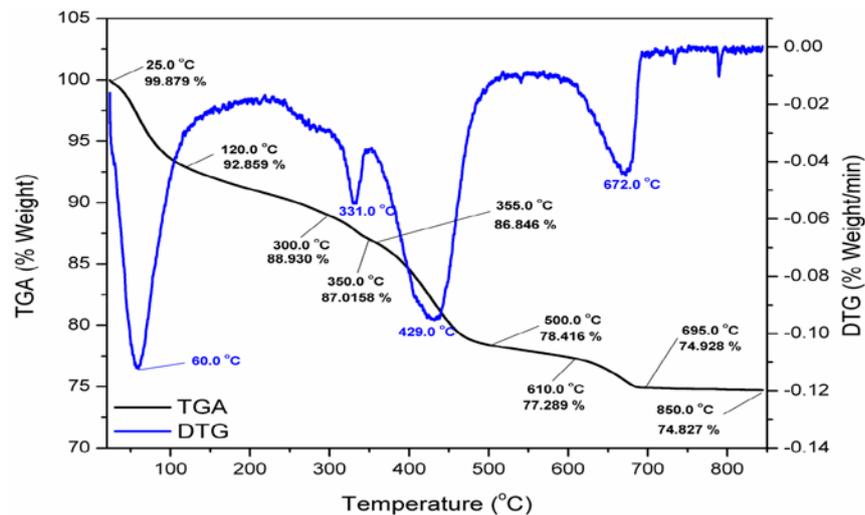


Fig. 6.2: TGA and DTG curves of CZBFA

### Zeolites from BFA and its derivatives

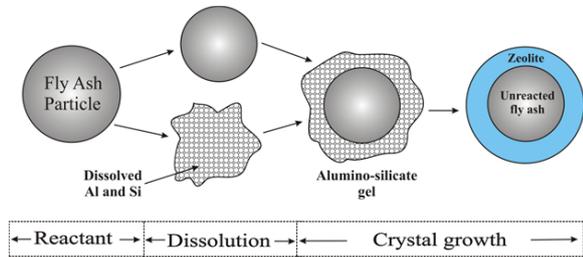
Diverse routes are used for transformation of the BFA into zeolites. The major methods of transformation of BFA into zeolites are as follows:

#### Hydrothermal treatment

BFA obtained from the sugar industry is washed thoroughly with double distilled water to eliminate the presence of foreign impurities and lighter particles. It is dried in sunlight for 8 h and

sieved through 200  $\mu\text{m}$  mesh sizes. The sieved materials are suspended into 3 M NaOH solution (10:1 liquid/solid ratio) in a 1 l round-bottom flask for alkaline hydrothermal treatment. It is refluxed for 72 h with intermittent stirring at a reaction temperature of  $373 \pm 5$  K for the preparation of zeolite bagasse fly ash (CZBFA). The resultant mixture is filtered and washed with double distilled water until the removal of excess of free sodium hydroxide and dried at  $373 \pm 10$  K in hot air oven. This zeolite synthesis is best described in schematic fig. 7 [17]. The dried zeolitic material (CZBFA) is sieved through 75  $\mu\text{m}$  mesh size sieve and stored in air

tight desiccators till their utilization of the sorption process. The sodium hydroxide added to the fly ash not only works as an activator but also adjusts the sodium content in the sorbent material [16, 17]. Hydrothermal treatment of BFA can be given in the presence of electrolyte (NaCl) by two methods: conventional and microwave heating.



**Fig. 7: Illustration of reaction mechanism for the batch hydrothermal conversion of fly ash to zeolites**

### Conventional heating

In Conventional heating, 200  $\mu\text{m}$  mesh sizes sieved material of BFA is suspended in a mixture of 0.5 M NaOH and 1.5 M NaCl solution (1:10 solid: liquid) in a round bottom flask. The resultant mixture is refluxed with intermittent stirring at  $373 \pm 5\text{K}$  for 72 h, thereby hydrothermal treatment is performed. Then after the reaction vessel is allowed to cool to room temperature and the suspension is filtered. The residual material is repeatedly washed with double distilled water for the removal of excess sodium hydroxide and sodium chloride by drying at 373 K in an oven for 6 h. The alkaline as well as electrolyte hydrothermal treatment successfully transformed BFA into conventional zeolitic bagasse fly ash (CZBFA) or electrolyte conventional zeolitic bagasse fly ash (ECZBFA) material [18].

### Fusion treatment of BFA

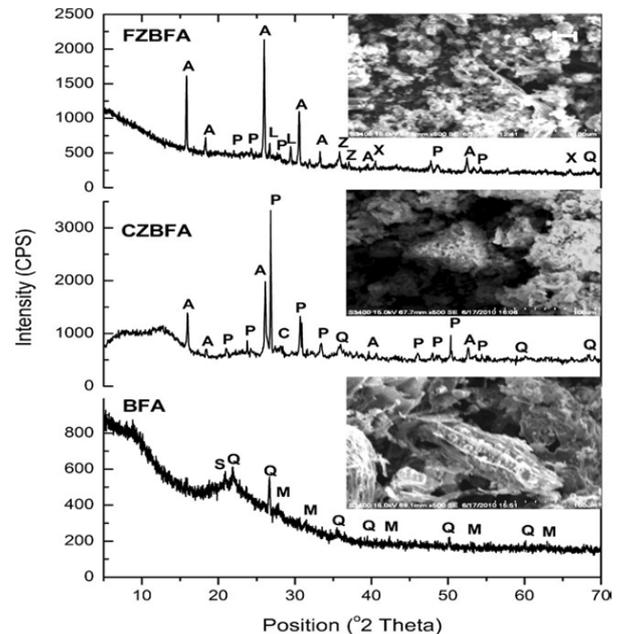
The dried BFA, 200  $\mu\text{m}$  mesh, is mixed and ground with sodium hydroxide in a predetermined ratio (NaOH/BFA = 1.2 w/w) to obtain a homogeneous mixture. The mixture is fused in a stainless steel crucible at  $823 \pm 10\text{K}$  for 1.5 h. The resultant fused product is cooled to room temperature, ground further and added to 128 ml of doubly distilled water. The slurry is agitated mechanically for 12 h at room temperature and then crystallized under static conditions at 363 K for 6 h. At the end of the process, the resultant solid is separated by filtration. Repeatedly washing with doubly distilled water will remove sodium excess hydroxide and the solid is dried at  $373 \pm 10\text{K}$ . The dried zeolitic material (FZBFA) is passed through a 90–120  $\mu\text{m}$  mesh sieve. The yield of the final product (FZBFA) is about  $82 \pm 5\%$ . The dried BFA and zeolitic materials (CZBFA and FZBFA) are stored in airtight desiccators until required [19].

Hydrothermal treatment of bagasse fly ash can effectively transform the zeolitic composition to a more specific mineralogical composition of various types of zeolites. Moreover, the morphology of glass phase undergoes the change with the development of crystallization.

The identification of corresponding crystalline and mineralogical characteristics of zeolite bagasse fly ash from powder X-ray diffraction (PXRD) patterns are made by comparing the diffraction data against a database provided by "Joint Committee on Powder Diffraction Standards" (JCPDS) and "International Centre for Diffraction Data" (ICDD). The PXRD patterns of BFA, CZBFA, and FZBFA, which shown in fig. 8 wide huge humps at a lower diffraction angle in the BFA diffraction pattern, indicates the presence of glass phase [20]. BFA exhibits the presence of  $\alpha$ -quartz peaks (JCPDS 5-490) with several small peaks of mullite (JCPDS 15-0776), a small peak of stilbite and other amorphous materials.

The PXRD pattern of CZBFA displays comparatively flat and low intense hump. Several new sharp diffraction peaks obtained in CZBFA which are not observed in PXRD of BFA. The observed newly intense

peaks at  $2\theta = 15.97^\circ$  and  $2\theta = 26.13^\circ$ , are ascribed to the formation of zeolitic units in CZBFA. The zeolite P (Phillipsite, JCPDS 39-0219), Analcime (JCPDS 76-0901), and Chabazite (JCPDS 12-0194) can be positively identified in CZBFA. Phillipsite (P) and analcime (A) zeolites covers the major part of synthesized zeolites with d-spacing values of 6.95, 4.22, 3.74, 3.66, 3.32, 2.89, 2.68, 1.97, 1.89, 1.80, 1.71, 1.68 and 5.54, 4.82, 3.41, 2.27, 2.22, 1.74, respectively [20].



**Fig. 8: PXRD patterns (X zeolite X, Z ZSM 12, L zeolite A, P phillipsite, Analcime, C chabazite, Q  $\alpha$ -quartz, M mullite, S stilbite) and SEM micrographs ( $\times 500$  magnification) of BFA, CZBFA, and FZBFA (10  $\mu\text{mscale}$ )**

Hydrothermal Conventional Zeolite Bagasse Fly Ash (CZBFA) and alkaline Fused Zeolite Bagasse Fly Ash (FZBFA) are characterized by PXRD technique. The FZBFA shows more intense peaks with total elimination of glass phase. The FZBFA is more crystalline than CZBFA. The SEM photographs of BFA exhibits amorphous and fibrous nature while FZBFA is more porous with large surface area.

### Microwave heating

Microwaves lie in the electromagnetic spectrum between infrared waves and radio waves. They have wavelengths between 0.01 m to 1 m and operate in a frequency range between 0.3 to 30 GHz. The typical bands for industrial applications are  $915 \pm 15\text{MHz}$  and  $2450 \pm 50\text{MHz}$ . Near 2450 MHz, the microwave energy absorption of liquid water is maximal. Interaction of dielectric materials with microwaves leads to dielectric heating due to a net polarization of the substance. There are several mechanisms which are responsible for this phenomenon including electronic, ionic, molecular (dipole) and interfacial (space-charge) polarization. In the presence of an oscillating field, dipolar molecules try to orient themselves or be in phase with the field. However, their motion is restricted by resisting forces (inter-particle interaction and electric resistance) which control their motion and generate heat.

Generally, materials can be classified into three categories based on their interaction with microwaves: (1) materials that reflect microwaves are categorized as bulk metals and alloys e. g. copper; (2) materials that are transparent to microwaves are fused quartz, several glasses, ceramics, Teflon, etc.; and (3) materials that absorb microwaves which constitute the most important class of materials for microwave synthesis, e. g. an aqueous solution, a polar solvent, etc. Dissipation factor which is a ratio of the dielectric loss to the dielectric constant is used to predict materials behavior in a microwave field. The microwave absorption ability of material is directly proportional to its dissipation factor [21, 22].

For microwave heating synthesis, 200  $\mu\text{m}$  mesh sizes sieved material of BFA is suspended in a mixture of 0.5 M NaOH and 1.5 M NaCl solution (1:10, solid: liquid) in a microwave refluxing system containing a flat bottom flask. The resultant mixture containing BFA is irradiated with frequency 2450 MHz frequency, corresponding to a wavelength of  $12.2\text{ cm}^{-1}$  for 15 min. The 15 min time is selected on the bases of trial experiments. After treatment time, the resultant suspension was filtered, repeatedly washed with double distilled water for the removal of excess sodium hydroxide and sodium chloride and dried at 373 K in an oven. The resultant synthesized zeolitic material is termed as electrolyte microwave zeolitic bagasse fly ash (EMZBFA). The dried material (EMZBFA) is ground to fine powder, sieved through 75  $\mu\text{m}$  mesh size and kept in plastic air tight containers [23, 24].

For microwave treated bagasse fly ash (MZBFA), the presence of zeolite is confirmed from the XRD pattern in accordance with the database provided by "Joint Committee on Powder Diffraction Standards". The XRD pattern of BFA shows the presence of glass phase. Fig. 7 demonstrate that the BFA exhibits the presence of  $\alpha$ -quartz (JCPDS 5-490) as a major part and other amorphous materials. The XRD pattern of MZBFA exhibits several new and sharp diffraction peaks that are not present in BFA. The newly observed intense peaks at  $2\theta=26.54^\circ$  and  $2\theta=43.09^\circ$  can be the significance of zeolite formation in MZBFA. Zeolite P (Phillipsite, JCPDS 39-0219) and Zeolite X (JCPDS 28-1036) are found to be dominant in zeolite formation during hydrothermal treatment and can be seen in fig. 9 [25]. The other crystalline phases identified in the MZBFA are Analcime (JCPDS 76-0901), Zeolite A (JCPDS 14-90), Chabazite (JCPDS 12-0194) and ZSM 12 (JCPDS 15-274). The PXRD pattern thus changes of Quartz to Philips sites. Their total disappearance of the Quartz mineral [25].

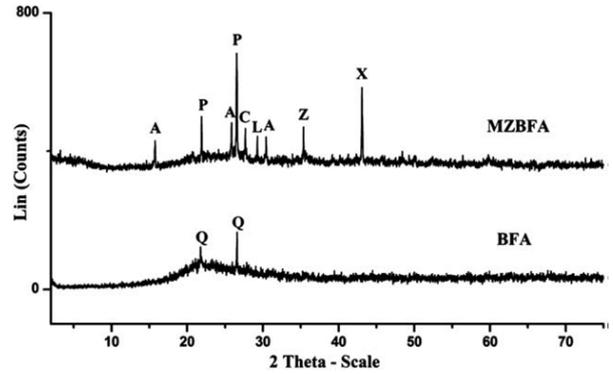


Fig. 9: PXRD patterns of BFA and MZBFA, P=Phillipsite, X=Zeolite X, A=Analcime, L=Zeolite A, Z=ZSM-12, C=Chabazite, Q= $\alpha$ -quartz

The primary constituents of sorbents are well characterized by XRF data. The BFA contain a higher amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  content which is decreased gradually in zeolitic materials (table 1) [26]. During hydrothermal treatment for the preparation of zeolitic materials, the raw materials (BFA) having a higher amount of silica and alumina, were dissolved and produced aluminosilicate gel (white gel like material) this is due to the dissolution of glass phase (aluminum-silicate) into the alkaline solution. The sorbent ECZBFA has a higher amount of  $\text{Na}_2\text{O}$  and Cl than that of the CZBFA and BFA due to the electrolyte addition (NaCl) and enhances the sodium content. The other oxide content like  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  are found higher in zeolitic materials [26].

Table 1: Instrumental characterization of sorbents (BFA, CZBFA and ECZBFA)

Constituents	BFA	CZBFA	ECZBFA
MgO (%)	0.80	3.00	4.10
$\text{Al}_2\text{O}_3$ (%)	16.9	13.9	14.2
$\text{SiO}_2$ (%)	63.1	47.4	42.2
Cl (%)	3.00	2.70	3.20
$\text{K}_2\text{O}$ (%)	3.27	1.90	0.38
$\text{CaO}$ (%)	3.50	12.5	14.8
$\text{TiO}_2$ (%)	0.34	1.70	1.50
MnO (%)	0.12	0.44	0.56
$\text{Fe}_2\text{O}_3$ (%)	4.40	10.04	11.12
$\text{Na}_2\text{O}$ (%)	4.57	6.42	7.94

### Modification of zeolites

Zeolites were first identified as natural minerals having unique physical adsorption properties. From the years, 1845 to 1937 many researchers investigated the hydrothermal conversion and synthesis of silicates. Although there are a number of claims that zeolites had been made synthetically, they are unsubstantiated as identification was based upon chemical analysis and optical observations. Later attempts at reproducing these early experiments did not give identifiable zeolites. In 1940 Professor Richard M. Barrer found the necessary conditions for making zeolites synthetically, and he identified them by X-ray powder diffraction. By reacting the powder minerals leucite and analcime with aqueous solutions of barium chloride at temperatures of 180–270  $^\circ\text{C}$  for two to six days, a synthetic chabazite was obtained. In 1948, Professor Barrer synthesized zeolites entirely from synthetic solutions of sodium aluminate, silicic acid and sodium carbonate [10, 11, 27]. Thus, the followings are some of the routes used for modification of zeolite to enhance or change surface characteristics, a structure for a specific purpose.

### Magnetically modified

5 g of zeolite with a 6.1 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 4.2 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is mixed and dissolved in 100  $\text{cm}^3$  using ultrasonication. Thereafter the pH of the mixture is adjusted to 10.0 using 0.1 M NaOH, and the mixture is agitated in a rotary shaker at room temperature for 24 h. A total of 25 ml 6.5 M NaOH is then slowly added and mixed with the above solution. The solution is mixed for an 1 h after the addition of NaOH.

The black precipitates obtained are washed with ultrapure water several times with the assistance of an external magnetic field. This procedure leads to the formation of  $\text{Fe}_3\text{O}_4$ -zeolite nanoparticles with a size of around 10–20 nm. PXRD patterns are shown in fig. 10 [28]. The  $\text{Fe}_3\text{O}_4$ -zeolite is then oxidized in air at 300  $^\circ\text{C}$  for 3 h to obtain magnetically modified zeolite [28].

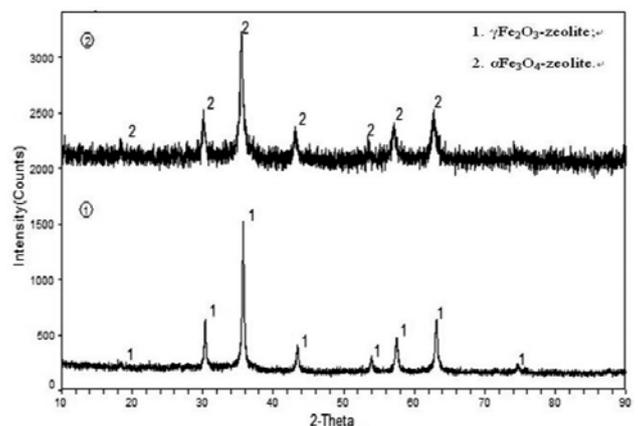


Fig. 10: PXRD pattern of  $\text{Fe}_3\text{O}_4$ -zeolites

### Surfactant modified

20 g of powdered zeolite and 170 ml of 0.06 M HDTMA-Br solution is placed in a 500 ml bottle and shaken at room temperature for 10 h, a time sufficient to reach adsorption equilibrium.

The mixture is then centrifuged, and the solid is washed with distilled water in order to remove unreacted monomers. The material is then completely air-dried prior to further use and fig. 11 shows the PXRD patterns of the Surfactant modified zeolite [29].

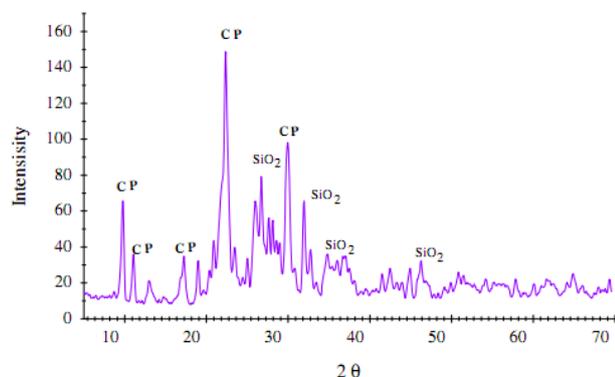


Fig. 11: PXRD pattern of surfactant modified zeolites Si/Al ratio modification

### Preparation of silicate and aluminate solution

The aqueous silicate solution is prepared in a plastic bottle by dissolving an appropriate quantity of rice husk ash or rice husk in 2 M NaOH or KOH solutions. The dissolution of the silica is very slow at room temperature, so it is assisted by heating the sample in an oven at 70 °C for 1 w and then filtered. Aqueous aluminate solutions are made by dissolving suitable amounts of sodium aluminate,  $\text{NaAlO}_2$  (61.3 wt% of  $\text{Al}_2\text{O}_3$ ) in doubly distilled water.

### Aluminosilicate solutions or gels

Aluminosilicate solutions or sol gels obtained by mixing the freshly prepared sodium aluminate and alkali silicate solutions in the correct proportions for the investigations. After mixing, the solutions or sol gels are usually allowed to equilibrate for 2 d at room temperature (25 °C). The solutions were made with the initial composition of  $2\text{SiO}_2:\text{Al}_2\text{O}_3:2\text{NaOH}$  and  $2\text{SiO}_2:\text{Al}_2\text{O}_3:2\text{KOH}$  for the synthesis NaA and analcime zeolite respectively.

### Zeolitization

Crystallization of zeolite is carried out by the two methods: (1) conventional hydrothermal method and (2) microwave-assisted method i.e. 2 h irradiation with a microwave (Panasonic NN-K543WF 1000 W) and then heating with hydrothermal method. In

this method, the resulting gel or solution of aluminosilicate is placed in a Teflon vessel inside the stainless steel reactor and heated in an air oven at different desired temperatures after irradiation with microwave for 2 h (which is an optimum time obtained in our investigation). At the end of this period, the reactor is cooled at room temperature to stop the crystallization. The product is removed, filtered and washed with distilled water before drying at 105 °C overnight. The procedure is repeated by changing the molar ratio of Si/Al in the range of 1–50. The synthesized zeolites were tested with PXRD (fig. 12) [30].

### Deployment of zeolites for the removal of pollutants from wastewater

Zeolites are intensively used for the removal of pollutants from wastewater. The pollutants broadly can be categorized by organic and inorganic pollutants. These pollutants disturb the natural balance of the environment.

Nature has provided plenty of resources that are used to sustain and develop life on the planet. One of the most important resources available to us is water. According to a World Health Organization fact sheet and other sources of the total amount of water present on the earth, 97.5 % is salt water and cannot be used without treatment. The remaining water (2.5 %) is generally fresh, but most of it (70 %) is locked in polar ice caps and glaciers, and the rest is mostly present as soil moisture or lies in underground aquifers. The fresh water that is available for use is 1 % or 0.007 % of the total water on earth. The search for clean, fresh, and potable water has always been one of the mankind's priorities [31]. Water quality has been influenced by the discharge of industrial wastewater, domestic sewage and agricultural pollutants [32].

There has been increasing concern about the released organic and inorganic compounds in the environment as a result of various industrial, agricultural activities, due to the potential toxic, carcinogenic and mutagenic effects of these substances. Organic compounds such as phenols, dyes and nitro aromatics are considered to be hazardous wastes which are released into the aquatic environment by industries such as coke ovens in steel plants, petroleum refineries, phenolic resin, fertilizer, pharmaceutical, chemical and dye industries [33,34]. Inorganic pollutants such as ammonium, copper, cadmium and lead from rooftop runoff water [35], the presence of various hazardous contaminants like fluoride, arsenic, nitrate, sulfate, heavy metals and other elements in ground water or surface water make the water unsafe and dangerous for the drinking purpose [36]. A fundamental requirement for safe human life and protected green environments is mainly based on the abundance of clean, uncontaminated water.

Adsorption is one of the most effective processes of advanced wastewater treatment, which industries employ to reduce hazardous organic and inorganic wastes in the effluent [37].

Here discussed below organic and inorganic pollutants of the environment and their removal by bagasse fly ash and its derivative zeolitic materials.

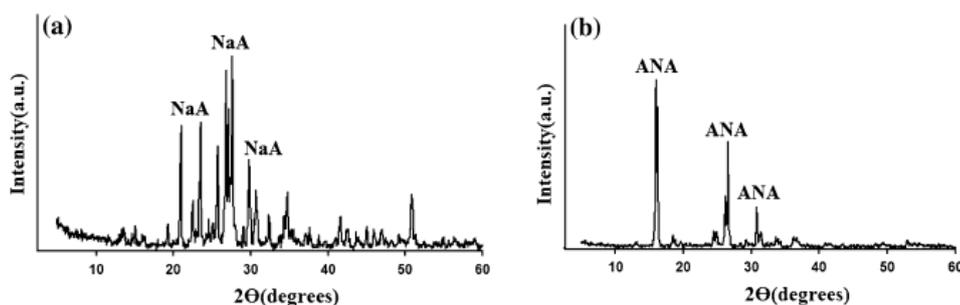


Fig. 12: PXRD pattern of NaA and analcime (ANA) zeolites

## Organic pollutants

### Pesticides

Bagasse fly ash is used for removal of DDD [2,2-Bis (4-chlorophenyl)-1,1-dichloroethane] and DDE [2,2-Bis (4-chlorophenyl)-1,1-dichloroethene] pesticides from wastewater. In batch experiments, DDD and DDE are removed up to 93 % at pH 7.0, with an adsorbent dose of 5 g/l having particle size 200-250.25  $\mu$ m at 30 °C. In column experiments, removal of these two pesticides is achieved up to 97-98% at a flow rate of 0.5 ml/min. Bagasse fly ash also adsorbed lindane and Malathion from the waste water up to 97-98 % under optimum conditions (equilibrium time 60 min, pH 6, adsorbent dose 5 g/l and particle size 200-250.25  $\mu$ m). The material exhibits good adsorption capacity and follows both Langmuir and Freundlich models. Thermodynamic parameters indicate exothermic process [38, 39].

### Phenols

Phenol is an important component of the wastewaters emanating from many industries, notably the petrochemical, oil refining, coal tar, plastics, leather, paint, pharmaceutical, steel and pesticide industries. The contamination of drinking water by phenolics at concentrations as low as 1.0 g/l brings about significant taste and odor problems, making the water unfit for use [40]. Bagasse fly ash is one of the low-cost adsorbents for removal of phenol from the waste water.

Wastewater obtained from a coal gasification plant is successfully treated on the columns of this adsorbent material like BFA. The effluent is treated with a mild acid allowed to settle down for some time in a tank and then fed to columns of adsorbent. Almost complete removal of phenol from 50 ml of wastewater at pH 4.0 is possible with the column of bagasse fly ash (particle size 200-250  $\mu$ m mesh; adsorbent dose 4.0 g; rate 4 ml min<sup>-1</sup>) [41].

The adsorption of phenol on BFA, CZBFA and FZBFA was performed to evaluate the influences of various experimental parameters like initial pH, contact time, adsorbent dose and initial concentration and temperature. No significant change was observed in the uptake of phenol up to 8.0 pH, after that uptake dropped down gradually (fig. 13) [17].

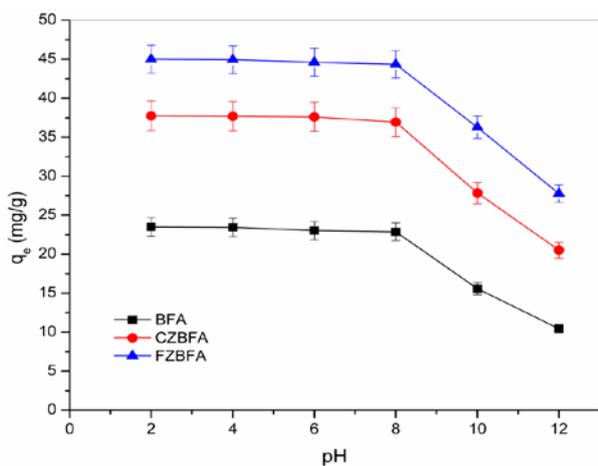


Fig. 13: Effect of pH on sorption of phenol by studied sorbents

### Dyes

Dyes are a kind of organic compound with a complex aromatic molecular structure that can bring bright and firm color to other materials [42]. The color is the most obvious indicator of water pollution. The discharge of colored wastes into receiving streams not only affects the aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic activity. Dyes and pigments are emitted into wastewaters mainly from the dye manufacturing and textile finishing. Wastewaters offer considerable resistance for their

biodegradation due to the presence of heat and light stable dyes, thus upsetting aquatic life. Hence, the conventional methods in sewage treatment, such as primary and secondary treatment systems, are unsuitable. The adsorption process provides an attractive alternative treatment [43]. Hence, bagasse fly ash is the best alternative.

The adsorption of brilliant green (BG) on carbon rich bagasse fly ash (BFA) batch studies are performed to evaluate the influences of various experimental parameters like initial pH, contact time, adsorbent dose and initial concentration on the removal of BG. Optimum conditions for BG removal are found to be pH 3.0, adsorbent dose 3 g/l of solution and equilibrium time 5 h. Adsorption of BG followed the pseudo-second-order kinetics. Intraparticle diffusion does not seem to control the BG removal process. Equilibrium isotherms for the adsorption of BG on BFA are analyzed by Freundlich, Langmuir, Redliche Peterson, Dubnine Radushkevich, and Temkin isotherm models using non-linear regression technique. Redliche Peterson and Langmuir isotherms are found to represent the data best for BG adsorption onto BFA. Adsorption of BG on BFA is favorably influenced by an increase in the temperature of the operation. The values of the change in entropy ( $\Delta S_0$ ) and the heat of adsorption ( $\Delta H_0$ ) for BG adsorption on BFA are positive. The high negative value of the change in Gibbs free energy ( $\Delta G_0$ ) indicates the feasible and spontaneous adsorption of BG on BFA [44].

The zeolite of bagasse fly ash synthesized from BFA by alkaline hydrothermal treatment is more effective for removing MB from aqueous solution compared with a BFA. Maximum sorption of MB by BFA and ZFA are found to be 71 % and 45 %, respectively, for removal of MB at 2 mM initial dye concentration with an adsorbent dose of 4 g/l in 60 min. The equilibrium data of MB sorption best fit to the D-R isotherm model for ZFA and Langmuir isotherm model for BFA.  $RL < 1$  obtained from Langmuir isotherm indicates favorable adsorption. Adsorption kinetics are best represented by a pseudo-second-order rate expression for sorption of MB on BFA and ZFA. BFA and ZFA effectively remove MB dye from water and cost less than commercial activated carbon [45].

## Inorganic pollutants

### Heavy metals

The term heavy metal refers to metallic elements with relatively high densities that are toxic at low concentrations. Heavy metals have atomic weights between 63.5 and 200.6 and specific gravity higher than 5.0. Heavy metals are classified into three main groups as toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru, etc.) and radionuclides (such as U, Th, Ra, Am, etc.). The main sources of pollution are mining and electroplating industries discharging a variety of toxic metals into soils and water bodies [46-50].

The results from the sorption of Cu (II) and Ni (II) show that the modified zeolitic sorbents ECZBFA has an excellent sorption capacity than that of CZBFA and BFA from aqueous solution within a time interval of 360 min. The experimental sorption isotherm data were well fitted by the Langmuir isotherm model indicating physisorption. The spontaneous and endothermic nature of the sorption process of Cu (II) and Ni (II) is confirmed by thermodynamics studies. The results of the kinetic data are revealed that pseudo-second-order kinetic model provided a good correlation coefficient data, and hence, it best fits the kinetic model. The sorption phenomenon of metals exhibits first external film diffusion and then undergoes an intraparticle diffusion process. The reagent 0.1 M HCl is better desorbing reagent and can be utilized for column desorption study [51]. The amount of metal uptake capacity ( $q_e$ ) was lower at acidic pH values but gradually increases as the values of pH increases. At low pH, the surface of the sorbents covered by hydronium ions, which decreases the metal interaction with binding sites of the sorbents by greater repulsive forces. As the pH value increases, the positive charge on the zeolitic sorbents surface decreases which enhanced the sorption capacity.

However, the maximum Cu (II) and Ni (II) uptake was observed at pH 5.0 and 6.0 respectively as shown in fig. 14 [52].

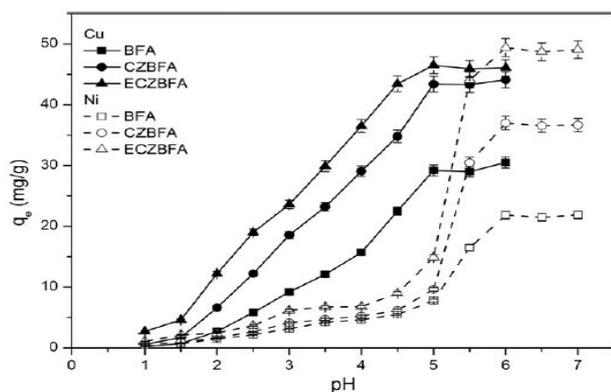


Fig. 14: Influence of pH on the uptake of metal Cu (II) and Ni (II) on sorbents

### Inorganic anions

To achieve the safe zone for the removal of arsenate and arsenite, the optimum conditions were as follows: As (V) and As (III) initial concentration of 80.0 and 70.0  $\mu\text{g/l}$ , respectively, pH 7.0, a dose of 3.0 g/l, a temperature of 20.0  $^{\circ}\text{C}$  and a particle size of 150–200  $\mu\text{m}$ . Adsorption data best fitted the Langmuir and Freundlich isotherms. Adsorption kinetics indicated that adsorption is controlled by the pseudo-first-order kinetics. The adsorption is found to be exothermic in nature. The negative value of  $\Delta G^{\circ}$  indicated spontaneous adsorption on BFA. The removal of both arsenic species is achieved up to 98.9 and 95.6 % by column operations at a flow rate of 1.0 ml/min while 95.0 and 89.5 % of arsenate and arsenite is removed in batch mode. The developed system for the removal of arsenite and arsenate is economic, rapid and reproducible [53]. Table 2 below exhibit the water treatments for various pollutants as sorbates with BFA and its derived/modified zeolitic sorbents [15-20].

Table 2: BFA derived zeolites used for removal of pollutants in wastewater

S. No.	Adsorbent	Pollutants
1	BFA	Phenol, 2-chlorophenol, p-nitrophenol, Reactiveblack-5, Brilliant green dye, Orange-G dye, Methyl Violet dye, methylene blue, Acephate, Phosphamidon, Lindane, Malathion, DDD [2,2-Bis (4-chlorophenyl)-1,1-dichloroethane], DDE [2,2-Bis (4-chlorophenyl)-1,1-dichloroethene]
2	CZBFA	Phenol, Reactive Black-5
3	ECZBFA	Cu (II), Ni (II), Pb(II)
4	MZBFA	Reactive Black-5, phosphamidon
5	FZBFA	Phenol, 2-chlorophenol, p-nitrophenol

### CONCLUSION

Bagasse fly ash is an agricultural waste which can be transformed into environmentally friendly, high-value zeolitic material using different methods of synthesis such as hydrothermal: this technique further can be classified as conventional and microwave heating. It can be used for making electrolyte; surfactant treated modified zeolites. The synthesized material is best used for environmental remedial action to remove organic and inorganic pollutants from wastewater in the mode of trapping the pollutant in the pore of the materials or void volume. It can also be used as ion exchange for metallic pollutants, the green catalyst in the synthesis. The used zeolite in pollutant removal is can further be used for making concrete and building materials. Thus, bagasse fly ash, and its derivatives are economic and environmental friendly which contribute great for natural ecosystem balance setting.

### CONFLICT OF INTERESTS

Declared none

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