MEDALION JOURNAL: Medical Research, Nursing, Health and Midwife Participation | ISSN(e): 2986-7754
Volumes 6 No. 2 (2025)

Review on Surfactant Modified Zeolites as slow Release fertilizer

Sabiya Khan[1], Sheikh Abdul Majid[2]
[1,2]Islamic University of Science and Technology
E.mail:khanarhaan31326@gmail.com

Received	: 17 February 2025	Published	: 16 April 2025
Revised	: 23 February 2025	DOI	: https://doi.org/10.59733/medalion.v6i2.183
Accepted	: 22 March 2025	Link Publish	: https://medalionjournal.com/index.php/go

Abstract

Zeolites could be the potential solution of some major problems in agriculture including pollution due to excessive use of fertilizers and economic drain due to the same. Ion exchange of zeolites can be used to load agents as well as release them and the high ion exchange capacity improves the loadings of agents. Because of these properties, zeolites have been used for controlled release of fertilizer components. Zeolites added to fertilizers help to retain nutrients and therefore improving the long term soil quality by enhancing its absorption ability. The surfactant modified zeolites (SMZ) could be used as carriers in controlled release formulations of fertilizer with higher affinity for anions to decrease its contamination potential.

Key words: ***Zeolite, Surfactants, Fertilizers.***

Introduction

A.F. Cronstedt, a Swedish mineralogist, heated an unknown silicate mineral in 1756 and noticed that upon rapid heating, this material produced steam from water. This result led him to call mineral zeolite (from the Greek words “zeo”for “to boil” and “lithos” for “stone”) [1].Zeolites are three dimensional crystalline silicates and aluminosilicate with clearly defined pores and cavities of molecular dimensions (Ca 3-12Å) within their structure [2]. In simpler words, they are solids with relatively open 3D crystal structures built from Al, O2 and Si with alkali or alkaline earth metals and water molecules trapped in gaps between them [3].These microporous materials have achieved great success as ion exchangers in the detergent industry, in the treatment of liquid waste, in the storage of radioactive waste, as catalysts for oil refining, in petrochemistry, and in the synthesis of organic compounds to produce fine chemicals [4]. However, Milton and Breck at Union Carbide in the 1950s produced the most important early synthesis breakthroughs from an industrial stanic. They created the reactive gel crystallization, which is now regarded as the standard method for synthesizing zeolites. [5].

1.1 Structure of zeolite

The two most abundant elements in the earth's crust, oxygen and silicon, are also the major elements found in the majority of zeolite minerals. The charge balance must be maintained, and the atoms must fit together to form a stable structure, which are the two most important principles in understanding zeolites. Zeolites are formed in the presence of water at low temperatures and pressures [6]. Zeolite has the empirical formula **MX/N [(AlO2)x(SiO2)y] .wH2O** where M = alkali or alkaline earth metal cations, n = cation valence, w = number of water molecules per unit cell, x and y = total number of tetrahedral per unit cell[7].

Zeolites are categorized as having 1:2 tetrahedral cation to oxygen ratio and a tetrahedral framework structure. In other words, every TO4 tetrahedron (T=Si or Al) shares every O with a tetrahedron that is next to it. Zeolites exist because one Si^{4+} and two O^{2-} can coexist in charge balance and because Si^{4+} and O^{2-} can be put together to form a framework. Al^{3+} ions replace some Si^{4+} ions, leaving the tectosilicate framework with a net negative charge. This change typically occurs on oxygen anion bound to an aluminiumcation and results from the formal valency difference between the $(AlO4)^{5-}$ and $(SiO4)^{4-}$ tetrahedrons [3]. Counterions, which are typically alkali or alkaline earth metals like Na, K, or Ca balance the resulting negative sites. The aluminosilicate structure is joined to these ions on the exterior surface of zeolite by weaker electrostatic bonds. [8].

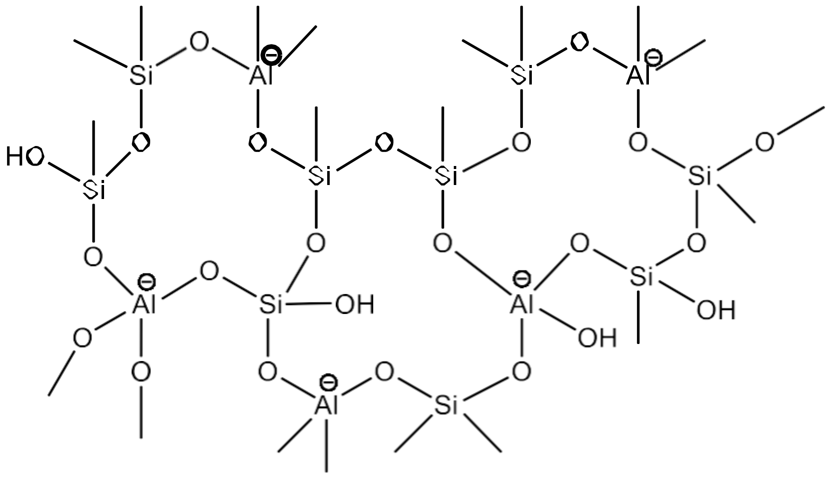


Figure 1.1: Two-dimensional zeolite framework [9].

Zeolites can be broadly classified as natural and synthetic zeolites [10].Among 200 types of zeolites available, 50 are naturally occurring and remaining 150 are synthetic zeolites. Rocks from volcanoes and sedimentary basins give rise to natural zeolites with common zeolites being clinoptilolite, chabazite and mordinite [11]. These were initially found in basalt cavities and vugs[12]. Natural zeolites were initially used in agriculture and as adsorbents. The production of natural zeolite and their sales were expected to reach 50000 and 40000 metric tons per year respectively. Natural zeolites have disadvantage of irregularities in their properties as they exhibit different chemical composition even obtained from same mine.On the other hand, synthetic zeolites are prepared from either raw materials obtained from nature such as kaolin or from synthetic raw materials such as silica and sodium aluminates [4]. Zeolite A, Y, X, and P are among the various varieties of synthetic zeolites [11]. Zeolite A, X and P were synthesized from coal fly ash and Municipal Solid Waste bottom ash. To maintain the silica to aluminium ratio, pure alumina and silica compounds such as aerosol powder and sodium aluminate were added [13].

Zeolites, both natural and synthetic, have many uses in industrial, biomedical, and agricultural processes [11]. To enhance the structure, pore size, and photocatalytic activity Cheng Wang et al. synthesized natural zeolite supported Cr-doped TiO2photocatalyst [14].It has been also observed that natural zeolites are more resistant to acidic environment and have greater thermal stability compared to synthetic zeolites [4].

1.2 Synthesis of Zeolite

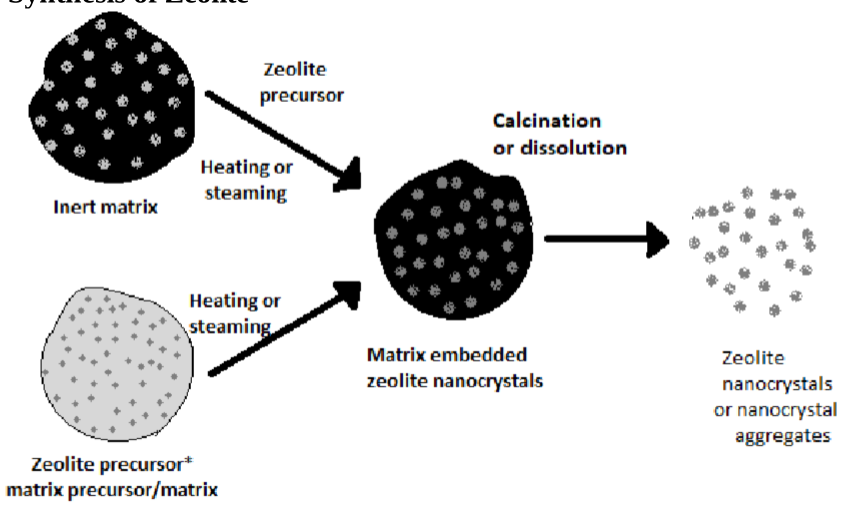


Figure 1.2: scheme for the confined space syntheses of zeolite crystals [15].

Most of the molecular sieve zeolites are synthesized in batch systems. The synthesis procedure involves the mixing of silica, alumina and distilled water in a beaker. Mineralizer is added to maintain alkalinity and a template (such as ammonium salt, amine and alcohol) is added as structure determining agent. After mixing, the solution becomes viscous due to formation of amorphous gel [16]. The gel is then transferred to autoclave and put into oven maintaining temperature above ambient (60-180°C) at pressure 1-50 bar for some hours to days for crystallization [17]. As the synthesis proceeds the formation of zeolite crystals occurs by nucleation step [16].

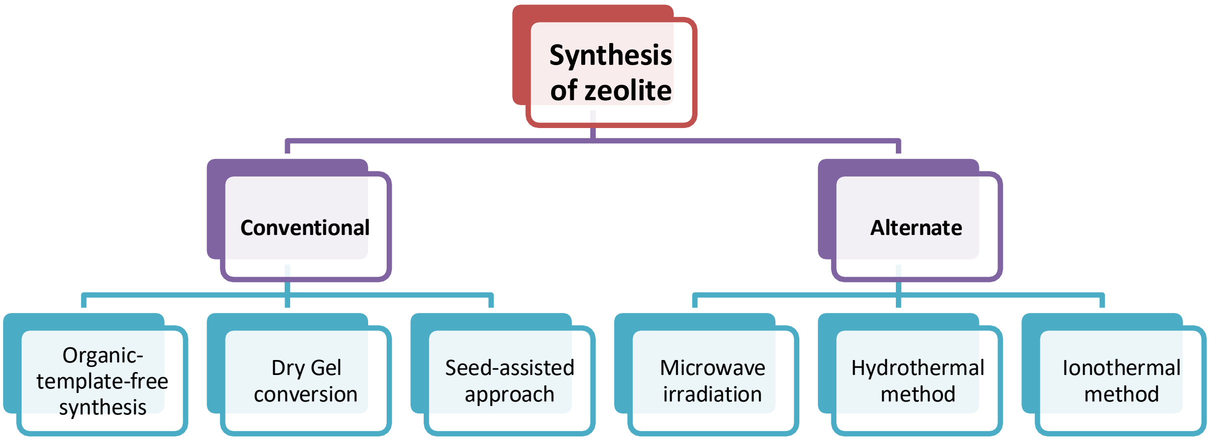


Figure1.3: Flow chart of various methods of zeolite synthesis

1.3 Various methods to synthesize zeolite are:

1.3.1 Organic template free synthesis:

This synthesis method can be scaled up and is economical and environmentally friendly. This synthesis produced nanoparticles made of zeolite Y (Y-NA) through one step crystallization method without using any organic template. The obtained zeolite is strongly acidic as well as it has micro-mesoporous structure. Furthermore, HY-NA demonstrated effective catalytic activity inRitter reaction [19]. Yi Haung et al. described a modified three-stage temperature control approach for synthesizing HY-NA without the need of organic additives, pore-forming agents, or crystal seeding. They created zeolite material with controlled mesoporousity and tunable size without significantly altering the size of zeolite crystals. [20]

1.3.2 Dry Gel conversion synthesis:

Dry gel conversion (DGC) synthesis of zeolite has many advantages like high yield, less waste, less usage of template etc. In this synthesis, the gel and liquid remains intact which may affect the nucleation and growth of zeolite, also the properties of obtained zeolite are affected [21]. This technique allowed for the usage of methylene bridged organic-inorganic hybrid zeolite without the use of any organic additives. CO^{2+} substituted hybrid zeolites were used in epoxidation of alkene. More crucially, because of its adjustable catalytic activity, methylene- bridged hybrid can be used in heterogeneous catalytic reactions. [22]. J. Weitkamp and M. Hunger synthesized zeolites Beta and EU-1 with different Gallium and Aluminium content. After increasing conversion timeframes, the zeolites [Ga] beta X-ray powder patterns revealed that long-range order was quickly formed during the first 16 hours of dry gel conversion. However, NMR spectroscopy revealed that the local structural change lasts for up to 65 hours. The local structure dry gel molecules began to rearrange when chemical bonds broke down, which increased the concentration of the defect SiOH group as evidenced by ^{1}H MAS-NMR spectroscopy [23].

1.3.3 Seed-assisted approach:

This synthesis was discovered to be an easy and practical method for breaking the crystal habit. The characteristics of the seed were shown to have a considerable influence on the finished result. This synthesis varies from classical procedures in that the tendency of the seeds to dissolve results in an unknown memory of the seed crystal structure, which makes it easier for the product to crystallize [24]. ZSM-22 zeolite was created by Lenivaldo V. de Souse Junior et al. utilizing crystallization seeds and an inexpensive source of silica. They looked at how the properties of the zeolite that was produced were affected by the inclusion of methanol as an organic solvent, the Si/Al ratio, alkalinity, the addition of K^{+}, and agitation. The seeds were created using a hydrothermal technique at 160 °C with an organic template made of 1,6- diaminohexane. [25]. Hiroyuki Imai et al. created the CHA type zeolite from amorphous aluminosilicate gel in absence of organic structure directing agents using seed assisted method. The seed assisted approach was found to decrease the crystallization period to 24 hours. By reducing the total amount of alkali cations supplied and substituting cesium for potassium, the Si/Al ratio of the CHA zeolite was raised. [26].

1.3.4 Microwave Irradiation:

It is the most typical technique for zeolite synthesis. To create a homogenous mixture for microwave irradiation, various Al/Si ratio, source, and structure-directing agent are mixed together. The size, shape, and temperature of the autoclave, together with the reaction duration and microwave temperature, can all be adjusted to control the reaction. [27]. In many cases this synthesis has proven that synthesis time can be remarkably reduced. LTA, AFI, FAU, ETS-4, SOD etc. types of zeolite membranes have been synthesized successfully by microwave irradiation [28]. BoitumeloMakgabutlane used microwave irradiation to create sodalite zeolite from coal fly ash biomass. Additionally, they noted that raw coal fly ash is ineffective as an adsorbent for ammonium in urine and solution. Also natural zeolite exhibited less ammonium removal efficiency compared to unadulterated phase sodalite with comparatively high surface area [29].

1.3.5 Hydrothermal method:

Hydrothermal synthesis method of zeolite comprises of two steps:Hydrated aluminosilicate gel is formed in the first step, followed by the crystallization step. The crystallization stage has 4 steps: (1)by dissolving amorphous aluminium and silicate in water with acidic or alkaline medium, a sol gel was created. (2)In an autoclave, the sol gel mixture was heated to create ordered subunits. (3) During the nucleation stage, a long-range order zeolite was created. (4) Formation of well grown crystalline zeolites. Predictably, aluminosilicate gels are crystallized as part of the hydrothermal process which consists the mixing of aluminate and silica solution with 1M NaOH, KOH and organic bases.The liquid was then homogenized by stirring it at room temperature. The nature of zeolite and its synthetic type are influenced by a number of variables, including the Si and Al composition, temperature, reaction duration, and reaction mixture pH [30]. Through the hydrothermal technique, Nyankson et al. created Zn-exchanged zeolite A from Al and Si based deposits. According to the findings, zeolite A was created with a cubic structure, and structural variations are dependent on batch formulations. They came to the conclusion that this approach needs a long period of crystallization—roughly 7 hours—to produce zeolite [31].Using a hydrothermal method, G.M. Arifuzzaman Khan and colleagues created the aluminosilicate zeolite Linde type-A from sodium metasilicate and aluminium powder. By adjusting various factors including crystallization time and temperature, agitation etc the surface acidity of the produced LTA zeolite was altered. They arrived at the conclusion that LTA zeolite can be employed as a catalyst in the production of petrochemicals. [32].

1.3.6 Ionothermal method:

In this synthesis, zeolites as well as other inorganic and inorganic-organic hybrid materials are prepared using a unique technique. Ionic liquids are used in Ionothermal synthesis to create zeolite by acting as both a solvent and a structure-directing agent. Ionic liquids containing low concentration of water behave differently to other solvents with comparable moisture levels due to which the synthesis involves lower hydrolysis and also the chemical composition of product will be different from the normally prepared product through hydrothermal method [33]. In [emim] Br ionic liquid and a urea-ChCl deep eutectic solvent, Yasong Wang et al. produced ZIF-67, ZIF-8, SOD, Zni-type zeolite, among other materials. The ZIFs dissolve in the ionic liquid and then precipitate out of the solvent as a result of cooling-induced crystallization. They noticed that the product's morphology is affected by the cooling rate. [34].

1.4 Application of zeolites

1.4.1 Application of Zeolite as catalyst

Zeolites have catalytic properties because their active sites are present in the OH bridging framework between silicon and aluminium channels. [11]. J.E Naber et al. have found the application of Zeolite as Catalyst in petrochemical industry and in oil refining .The development of Zeolite Catalyst is increasingly supported by advances in preparation, characterization and testing of catalyst for the determination of property relationship [35].Zeolites are utilized as catalyst in several significant refining processes, including as olefin alkylation, light naphtha isomerization, cracking, , reforming, and hydrocracking. [36]. Bilge Yilmaz et al. found the catalytic application of zeolite in chemical industry. They stated that because of current and potential application of zeolite in catalysis. It plays great role in quest for raw material change [37]. Andreas Martin and Coworkers reported the manufacture of new hierarchical composites including ZSM-5 and their application in the catalytic cracking of biomass rich in triglycerides to reduce olefins. They performed the experiment on fully automated SR-SCT-MAT at 550^0c with catalyst to oil mass ratio (0-$1.2g^{-1}$) [38]. HoubingZou and coworkersreported on the simple synthesis of a TSI@ mesosilica composite with a yolk/core shell structure, the catalytic capabilities of which were examined in the difficult hydroxylation of phenol. The catalytic analysis revealed a hierarchical pore structure with meso channels and micro pores and a large surface area of 560-700m^2/g. The synthesized solids exhibit increased activity at comparable selectivity when compared to the well-known TS-1. These composites demonstrated a better level of Para-product selectivity. [39]. GherardoGliozzi et al. reported that Zeolite was used as a catalyst to benzoylate phenol with benzoic acid, producing hydroxybenzophenone, which are crucial in the chemical industry. H- Y solids perform less favorably than H-Beta zeolites. It was found that the reaction process ignores the fries rearrangement of phenyl benzoate and instead forms hydroxybenzophenone by an intermolecular reaction between phenol and ester. [40]. YoungWang et al. documented the influence of dealumination and desilication on Beta zeolite and were used as a catalyst in the conversion of n-hexane to propene. HNO3 therapy was used for dealumination and alkali treatment produced desilication. After alkali and then acid treatments, the selectivity for propene and catalytic stability at high n-hexane conversion increased. 1) The fewer acid sites were the cause of this increase. 2) Increase in mesopores which were advantageous to the diffusion of coke precursor mixtures [41]. Jing Han et al. reported on the production of 87.6% Ga_2O_3 / ZSM-5 hollow fibers as dehydrogenation catalysts to convert n-butane into light olefins and aromatics at 600^0c. The results showed that a very small amount of Ga can significantly increase the catalytic activity of ZSM-5 due to a synergistic interaction between Ga_2O_3's dehydrogenation and aromatization properties and ZSM-5's cracking ability. [42].

Gouzhu Liu and colleagues demonstrated the catalytic capabilities of Pt/H-ZSM-5 in the conversion of phenol- and xylene-based compounds derived from lignin. The methylation of m-cresol into xylenols followed by hydrodeoxygenation to produce P-/m-xylene and the hydrodeoxygenation of m-cresol into toluene followed by methylation to produce p-/m-xylene are the processes that increase xylene yields when methanol is added. [43]. N.Fattahi et al.stated the catalytic role of zeolites in the manufacture of biodiesel through transesterfication reactions in processed soybean oil which contain triglyceride ester of both unsaturated and saturated FFA. In this study, through ion exchange procedure La/beta-zeolite was synthesized and used as a catalyst for soybean oil transesterfication [44].

Corma et al. reported that activated and deactivated activity of catalyst was strongly reaction dependent and also depend on numerous factors like temperature, pressure, metal loading, particle size etc. It was summarized thatatom migration takes place through cavities between two porous zeolite sites.Authors reported that; a) there may be change in metal atomicity from isolated metal atom to cluster. B) Supported single atom alloy may undergo potential structural transformation. C) By using the proper reaction conditions, single atom alloy nanoparticles can be created from bimetallic nanoparticles with chemical separation. [45]. K.D Pandiangan and colleagues reported that zeolite A synthesized by sol gel method has the catalytic activity and was derived fromaluminium metal and rice husk silica. The structure of zeolite A was characterized by FTIR and XRD analysis. This zeolite was observed to exhibit catalytic property in transesterfication of castor oil [46]. BastienReiprich et al.reviewed the seeding-free production of zeolites Y and their catalytic activity in the cracking low density polyethylene. The use of growth modifier organosilane through Bottom up route and mesoporegen was combined to avoid a seeding-step.

The sample LY-0.225-H, out of all the layer-like zeolite Y samples, demonstrated the most effective catalytic activity in the cracking of LDPE. [47]. RadostinaDragomirova et al. studied the catalytic application of zeolite. The detailed review on zeolite membrane is centered on their ability to change the thermodynamic reaction equillibria. They furthermore showed that by using the zeolite membrane, shape selectively and purification problems can be solved. Based on membrane locations, the zeolite membrane was classified as:-1) spatially decoupled membranes .2)Both membrane and catalyst reactors.3) in close proximity to a catalyst-packed bed. 4) Membrane as capsule around catalyst core [48]. According to Li et al. poly lactic acid, which is lactide from lactic acid produced by microbes, has a catalytic property of zeolite. [49]. Tao Pan and colleagues conducted extensive research on hierarchical zeolites in order to increase the catalyst activity, particularly the lifetime for potential industrial applications. [50].

1.4.2 Application of zeolite in water purification:

Zeolite play an important role in water purification from number of sources involving industrial, natural, municipal wastes. The wastes may include metal ions (Zn, Co, Cr, and Ni) or liquids [11]. KarmenMargeta et al. have studied that the natural zeolites exhibit efficient performance on removal of metal ions from waste water. Their water treatment efficiency depends upon type and quantity of the used zeolite, particle size, contaminant concentration n, solution PH, temperature, pressure etc. This study involved the standard procedures like column or batch process [51]. NevinKoshy and Coworkers reported the fly ash zeolite for water treatment and other environmental cleanup projects. Also the fly ash zeolite was loaded by bacteria and used for heavy metal and phosphate removal [52]. M.M Rahman et al. studied the application of zeolite Y (Na-Y) for water filtration. Acid treatment was applied to rice husk ash to create zeolite Y, which was then utilized in the water treatment process. [53]. Maryam YousfGadhban and Coworkers studied the application of nano zeolites in water treatment. Nano

Zeolites were prepared from coal ash for removal of methylene blue from waste water using packed bed column. It was observed from packed bed experiment that nano zeolite leads to high quality adsorbent for methylene blue elimination. Also elimination of methylene blue decreases with increase in flow rate and initial concentration while it increases on increasing bed height [54]. Nan Jiang and Luuk c. Rietveld reviewed high silica zeolite for organic micro-pollutants removal from waste water including industrial chemicals, pharmaceuticals etc. It was included that hydrophobicity andhydrophilicity of surface are related to adsorption capacities of these OMPs. It was also observed that oxidative regeneration of zeolites occur [55]. Olga Nazarenkodiscovered the use of sakhaptinsk zeolite for the purification of ground water. He studied the efficiency of this zeolite in removal of Ca, Mg and Fe from ground water by using the x ray diffraction analysis, thermal analysis, FTIR etc. clinoptilolite was found to be a main phase of zeolite tuff. The removal efficiency by this experiment was found to be 93% for Mn, 63-100% for Ca^{2+} and 96-100% for Fe [56].

GrigoriosItskos et al.utilized flyash to create the zeolites which were then used to treat the water in lignite mines. They used two different samples of Si fly ash and exposed them to hydrothermal treatment,which results in the formation of Phillipsite and Thomsomite, at a fixed solid-to-liquid ratio and constant temperature. The absorbing capacities of these zeolites lead to removal of various heavy metals including Cadmium, Cr, Copper,Ni, and Zinc [57]. JafarAzamat and colleaguesreported the separation of heavy metal like Hg^{2+} from water using molybdenum disulphide membrane which was placed in aqueous ionic solution. Ions were separated from solution under high pressure. The results obtained from long time simulation gives idea about permeation of ion and water through pores. It was observed that permeation doesn't occur through small pores in absence of pressure.

Therefore external pressure was mandatory for ion rejection from aqueous solution [58]. MachaweMxolisiMotsa et al.prepared polypropylene-zeolite polymer and found its application in water purification. The ability of this fabricated zeolite was to extract heavy metals and substituted phenols from water solution which usually depended upon PH of solution, contact time and loading on zeolite. Pb^{2+} was found to be removed at 6.5-7.5PH, tricholoro phenol at 4-6 PH and ortho-nitro phenol at 2-6 PH [59]. Xutao Chen and coworkers established a simple robust household water treatment plant for removal of heavy metals. They used the filters made up of cloth and cotton to filter water and beverages. The cotton used in this work was combined with zeolite. It was observed that 8 liters of waste water could be transformed into drinking water and enabled the heavy metal removal to concentrations of below 5 ppb ($\mu g\ L^{-1}$). In addition to this they also observed that ZCT could be utilized for disinfection [60]. A. Haralambous and coworkers reported that zeolite namely clinoptilolite may be effectively used for the removal of ammonium ion. The clinoptilolite exhibited the exchange capacity of 2-2.7 meq/g clinoptilolite being less costly than other zeolites and the stability of its structure make it of great interest for waste water treatment [61]. Mohammed Kadhom and coworkers used metal organic from coworkers for desalination in water treatment UIO-66 and ZIF-8, composed of 1,4- benzenedicarboxylate and 2- methyl imidazole as linkers, having high hydrophilicity and stability were the most common MOFs used for water purification [62]. Danila S. Paragas et al. obtained zeolite from rice hull and used for nitrate removal from water. Rice hull was treated with water and 1M hydrochloric acid before ashing. Results showed that zeolite leads to decrease the nitrate concentration in water [63].

1.4.3 Application of Zeolite in agriculture

Ippolito et al.reported the application of zeolite in agriculture including soil moisture maintenance, neutrality of soil. Soil with zeolite decreases nitrification rate because of $NH9^{+}$ adsorption in zeolite frame work which may decrease the N leaching. They compared corn growth using simple urea fertilizer and zeolite containing urea fertilizer. It was shown that the corn yield increased in case of zeolite mixed urea fertilizer because of its high selectivity for $NH9^{+}$ and k^{+} [64]. Mumpton and Frederick reported that clinoptilolite has best selectively for k^{+} and $NH9^{+}$ and acts as slow release chemical fertilizer. Results showed larger yields of tomatoes, strawberries and peppers [65]. Syed Ali Akbar and Coworkers found application of zeolites for nutrient retention. They reported that some surface modified zeolites can hold nutrients like $NH9^{+}$ nitrate, phosphate, potassium and sulphate in their porous structure. They also reported their slow release fertilizer properties [66]. Caroline De Smedt and coworkers reported that Zeolite has been used to protect the crops. They observed that just like kaolin, particle film of zeolite could be applied to prevent pest and diseases. They also reported that zeolite acts as leaf coating product because of their honey comb framework and capacity for co2 sorption which makes them effective against fungal disease and insect pests [67]. O.H Ahmad et al. found the application of zeolite in maize cultivation. They performed an experiment and results obtained showed that inorganic fertilizers along with zeolite increased uptake of N, P and K and hence have efficient use in leaves stem and roots. They also reported that zeolite in cultivation of zea mays could be beneficial on acidic soils [68]. AyseGul and Coworkers conducted the experiment on lettuce plant in which they took two cultivars oflactuca sativavizbombola for autumn season and brogan for spring season in which they used perlite and clinoptilotie as growing media in different ratios. The results obtained from experiment concluded that zeolite addition led to enhance the plant growth and decreasing K leaching [69]. Alberto C. de Campos Bernarite and Coworkers described that Brazilian zeolite sedimentary rocks have been used as slow release fertilizers and soil conditioners. It was observed that zeolite present in Brazilian sedimentary rocks was stilbite with smectic clay mineral and quartz. They did the experiment using four crops i.e.andropogon grass, Lactuca sativa, lycopersicum, andOryza sativa. The outcomes obtained showed Nitrogen, Phosphorus and k containing zeolite behaved as slow release source of nutrients and crop production was also increased by 20% [70]. StanislvaTorma and Coworkers reported that natural zeolite have an impact on soil nitrogen dynamics. They monitored the sorption of cations Mg^{2+}, Mn^{2+}, Fe^{2+} etc in soil mixed with zeolite and in powdered zeolite. They reported that zeolite when added to soil has effect for several years and inhibits the loss of nitrogen from soil.

They also observed that after short time of zeolite application, there is decrease in nitrogen content in the soil because of zeolite's ability to fix $NH4^{+}$, but after several days or weeks it increased because of zeolite's gradual release of nitrogen [71]. EdytaBorosLajszner et al. found the application of zeolite to neutralize nickel in soil. They conducted a pot experiment on two soils with different levels of contamination with nickel containing oats plant. The results showed that activity of enzymeslike dehydrogenases, phosphatase, urease etc decreased in these soils that were contaminated with nickel. Also when zeolite was added the level of accumulationof nickel in oats decreased [72]. M.Noori and colleaguesreported the use of natural zeolite for salinity improvement and crop yield. The zeolite used was clinoptilolite and crop was Raphanussativus. They studied six different soil treatments and concluded with result that showed in presence of clinoptilolitethe soil quality and crop yield may be improved [73]. One of the researches was conducted to investigate the effect of natural Iranian zeolite on nutrient status of radish. It was observed that this zeolite also enhanced nitrogen and potassium concentration in shoot tissues [74].

1.4.4 Application of zeolite in pharmaceuticals

Both natural and synthetic zeolites found their application in pharmaceuticals industry. Most of the zeolites including clinoptilolite exhibited various activities and was also used for treatment of diarrhoea. It was also observed that zeolites are used in artificial kidney [75]. Adriana M. Vargas and Coworkers investigated the feasibility of natural zeolite modified with CTAB for diclofenac sodium release. X-ray fluorescence, scanning electron microscopy, thermogravemetric analysis, DTGA etc were done to characterize the surfactant modified zeolite [76]. Tamer Mohammad Salem Attia et al. studied the elimination of pharmaceutical and products for personal care (Naproxen, Gemfibrozil, Ibuprofen and Diclofenac-Na) fromliquid solution using magnetic nanoparticles coated zeolite (MNCZ). Interaction, initial PPCPs concentration and solution PH were some of the various sorption parameters studied for reaction optimization. It was found that the removal of PPCPs was effectively encouraged by decreasing PH. Additionally; the Freundlich isotherm equation provided the best fit for the PPCPs studied for adsorption on MNCZ. [77]

Review of literature of Surfactant Modified Zeolite as the Slow Release of Fertilizer

DeepeshBhardwaj et al. prepared modified surfactant clinoptilolite and montmorillonite using hexadecyltrimethylammonium bromide ($CH_3(CH_2)_{15}N(Br)(CH_3)_3$, HDTMAB and dioctadecyldimethylammonium bromide ($(CH_3(CH_2)_{17})_2N(Br)(CH_3)_2$, DODMAB). The study shows suitability of surface modified silicates as an effective system for adsorption of nitrate and controlled liberation of nutrients the adsorption isotherm follows Langmuir and Freundlich isotherm [78]. Naoko Zwingmann et al. prepared the synthetic zeolite namely mesolite (using caustic treatment of kaolin) at high temperature of 80-95^{o} C to increase the water and nutrient holding capacities of the sandy soils. Mesolite have surface area and cation exchange capacity of 9-12 m^2/g and 494 cmol (+)/kg respectively. Column chromatography technique had been used to investigate the effect of mesolite added to sandy soil. Experimental results revealed that due to addition of this synthesized zeolite (even in low concentrations) can reduce the leaching of $NH4^{+}$from sandy soil. Mesolite is very effective (11 times) to retain $NH4^{+}$ and also releases slowly so acts as slow release fertilizer [79]. Three different mixtures viz 30/70, 50/50 and 70/30 of Chabazite-rich tuff (SOR),mordenite-rich tuff (KIM) and commercial clinoptilolite-rich tuff (BLG), CEC (sodium acetate method) were used by Michael G. Stamatakis et al. to increase the nutrient holding efficiency of loamy soils and also act as (SRF) slow release fertilizer (by carrying out various leaching tests on loamy soil). By using sodium acetate method cation exchange capacity (CEC) of SOR, KIM and BLG were calculated as 92.2, 100.9 and 95.7cmolkg^{-1} respectively (and mixtures of the three zeolites have intermediate value). Different mixtures used showed different SRF values like 30/70 releases NH^{4+} very slowly in

29 days (1.7%) and BLG is effective for the retention of Mg^{2+} ions (slow release of Mg^{2+}-39%)[80]. T. Scott Perrin et al. used natural zeolite namely clinoptilolite and loaded with NH^{4+} (by 10days soaking in 1mole of $(NH4)2SO4$) to enhance the nitrogen retaining capabilities of sandy soil to regulate the plant growth and productivity. Another motive of this experiment was to reduce the surface and ground water $NO3^-$ contamination. Sweet corn (Zea mays L.) was used for the said experiment. They conducted two greenhouse plant experiments.

Experiment 1:- Sweet corn was planted in sandy soil in different pots enriched with fertilizer either ammonium sulphate (AS) or ammonium loaded clinoptilolite (A-Cp)[with one of three size ranges viz small, medium or large] at different rates of 112, 224 or 336kgNha^{-1}. Experiment 2:- All conditions were kept same except the rates- 112 or 229kgNha^{-1} were used. From the pots under study they compared leaching of $NO3^-$ and $NH4^+$, RGR (relative growth regulators), LAR (leaf area ratio) and NAR (net assimilation rate) among all fertilizers containing nitrogen. Experimental results revealed A-Cp will minimizes (less than 5%) nitrogen leaching (independent of rate and particle size of A-Cp) more effective than AS [81]. A surface modified zeolite namely aminopropyltrimethoxysilane (APTMS) was explored and used as a nanofertilizer and as slow release fertilizer for nitrogen from urea. This modified zeolite has decreased crystalinity and pore size (7.74 nm). It was experimentally verified that release of urea in absence of modified zeolite was 100% limit in 10 min observation time where as in presence of APTMS urea release was 100% up to 120 min observation time [82].

Zeolite (Analar, BDH) used as carrier to prepare nitrogen nanofertilizer. The thirty days incubation was done in-vitro (at field moisture condition) to explore the capability of prepared zeolite as controlled release fertilizer for nitrogen.Hexadecyltrimethyl ammonium bromide (HDTMABr) was used to modify the surface of zeolite. Solution of zeolite and HDTMABr was prepared in the ratio of 1:100 and then agitated for 9-10 hours at 150 rpm. Powder of surface modified zeolite was stirred with solution of $(NH4)2SO4$ (1M) for 8h, and then filtered and dried –this will lead to the formation of nitrogen loaded zeolite. Experiment was conducted on Ipomoea aquatica (Kalmi/ water spinach) plant and studied the effect of synthesized nano- fertilizer on its growth. Results revealed that nano-fertilizer accumulates higher quantity of nitrogen in plants, better cation exchange capacity and moisture retaining capability as compared to conventional fertilizer. Another advantage of this fertilizer is that it is very cost effective [83]. Source of zeolite was taken from Weifang district of China having cation exchange capacity of 0.35 mole kg^{-1}. Nitrogen and phosphorus fertilizer used for the modification of natural zeolite were ammonium chloride ($NH4Cl$), monoammonium orthophosphate ($NH4H2PO4$) and potassium sulphate respectively. Fertilizer sources were added to zeolite in the ratio 1:2. Stirred mixture for 5 min for every 1-2h (process repeated 2-3 times) and then kept mixture for overnight to settle.

This N and K loaded zeolite was then used for cultivation of spinach. Experimentally proved that the yield of spinach increases significantly as compared to fertilizers without zeolite [84]. R. Malekian et al. studied the efficiency of naturally occurring clinoptilolite (Cp) and surface modified clinoptilolite to decrease leaching of $NH4^+$ and $NO3^-$ from agricultural land. Cp is negatively charged with positively charged counter ions which makes it a good cation exchanger. HTMABr modification on Cp surface increased its external cation exchange capacity (ECEC). HTMABr adsorbs as bilayer on surface of Cp below which Cp exchanges its charge results its higher efficiency, sorption and anion exchange capability. Field studies showed that Cp have ion exchange capacity of 11mg/g $NH4^+$ and surface modified (SMZ) Cp exchanges up to 800mmol/kg of $NO3^-$.These results indicates Cp and SMZ-Cp are suitable for controlled release of nitrogen [85]. Amit Kumar along with others, modified zeolite-A using hexadecyltrimethylammonium bromide (HDTMABr-cationic surfactant) to enhance its ability to hold anion of PO^{3-} (phosphate).

Fertilizer KH PO was used to load Zeolite-A and HTMABr modified zeolite-A with phosphate. Surface modified zeolite-A showed enhanced phosphorous loading by 4.9 as compared to zeolite-A. Experimental results showed that modified zeolite-A releases phosphorous with continuous percolation even after 1080h, however $KH2PO4$ can supply phosphorous hardly up to 265h under same conditions- this indicates that SMZ has adsorption affinity for P than conventional fertilizer, so can be used as SRF [86]. Hongxu Zhou et al. synthesized a zeolite from coal bottom and fly ash. Bottom and fly ash were first pellatilized (pellet mixture-60% fly/bottom ash+30% lime+10%clay) and used these bottom ash pellets (BAP) and fly ash pellets (FAP) to adsorb phosphorous. Studies revealed that the phosphorous adsorption ability of BAP is greater that FAP which makes it a better adsorbent of P. To enhance the adsorption of phosphorous on BAP and FAP a foaming agent cationic surfactant Sodium Dodecyl sulphate (SDS) was used. Different types of BAP and FAP with SDS were prepared at higher temperature of 700 C viz. FAP-0/BAP-0: 0% SDS, FAP-1/BAP- 1: 2% SDS, etc. SDS modification increased the porosity of FAP from 45.5% to 163.6% and of BAP from 52.9% to 76.5%. Increasing pH can also increase phosphorous adsorption [87]. This study involves the investigation of surface modified zeolite (SMZ) as slow release of nitrate. Zeolite material used as clinoptilolite (Cp) with particle size ranging in between 0.42 to 0.8mm and external cation exchange capacity (ECEC) of 100mmolkg^{-1}. HDTMABr was used for its surface modification. For determining the maximum ratio of sorption of nitrate to HDTMABr, Cp was modified by the said surfactant to 25%, 50%, 100%, 150%, 200% of its ECEC. Experimental data explored that HDTMABr modified Cp can show sorption of nitrate upto 80mmolkg^{-1}. Various tests like batch and column nitrate sorption, greenhouse tests proved that SMZ loaded with nitrate can be effectively used as controlled release of fertilizer (CRF) to reduce the nitrate loss form crop land [88]. Sheikh Abdul Majid et al. synthesized and modified the mordenite and Zeolite-A to study the sorption of $PO4^{3-}$ and $NO3^{-}$ on their surfaces. They studied the various factors affecting the sorption of ions under study like pH, temperature and concluded that adsorption of $PO4^{3-}$ and $NO3^{-}$ increases directly with increase in pH and temperature.

Experimental data showed that it took 12h to reach sorption equilibrium and also revealed that change in temperature not only influence but also results in change in thermodynamic parameters like standard Gibbs free energy, enthalpy and entropy [89]. Nano- particles of synthesized silicates (clinoptilolite and montmorillonite) and their surface modified forms were synthesized and studied as slow release fertilizer for phosphorous. Hexadecyltrimethylammonium bromide (HDTMABr) and dioctadecyldimethylammonium (DODMA) were used for modification of surfaces of these silicates separately. HDTMABr modified clinoptilolite and montmorillonite are called HC and HM respectively and DODMA modified clinoptilolite and montmorillonite are known as DC and DM respectively. Various experimental methods (Batch experiment, thin-layer funnel analytical test, soil column percolating system) used to study the effect of different parameters (temperature, pH, initial concentration of phosphate, adsorbent-adsorbatecontact time etc) on removal of phosphate. Results explored that HC showed high adsorption of P of 93.46 mg g^{-1} at pH 7 and concluded that modified zeolites or silicates are suitable for phosphorous adsorption and slow release because it can retain P upto 15 days of leaching [90]. This article involves the study of improving the nitrogen use efficiency (NUE) of nitrogen from urea using zeolite [Microporous natural zeolite (Z) and nanoporous zeolite (NZ)] as substrate. By impregnation of urea on substrate under normal conditions results in the formation of composite fertilizer. Adsorbent and commercially available urea fertilizer were mixed at different weight/weight ratios of 1:1 (showed high adsorption of 18.5 for Z and 28% for NZ) to 1:10 using hydrothermal method. Experimental data revealed that NZ and Z fused with urea releases nitrogen upto 48 days and 34 days respectively.

This indicates that NZU can releases nitrogen slowly and improves production of crop [91]. Kon, natural Bentonite (NB) and surface modified Bentonite (SMB) were used for the adsorption of pollutants and nitrogen, nitrate and phosphate respectively. At optimized conditions of pH (9) and dose for natural Bentonite was 233.3g/L and at pH 8 for SMB was 166.7g/L. NPK percentage in soil enhanced by 1.04%, 1.32% and 5.13% respectively after treatment of NB and for SMB it showed an increment of 1.30%, 2.25% and 6.18% respectively. These results indicate that SMZ can act as slow release fertilizer for NPK than NB [92]. Camilo Gomes Flores et al. used Brazilian coal ash for synthesis of potassic zeolites as controlled release of potassiumfor the production of wheat.

The preparation of this zeolite was done by using hydrothermal treatment (a conventional method) with KOH. A basic solution of 5M potassium hydroxide at 150 C for 24h (considered to be the optimum condition for zeolite synthesis. The zeolite so formed from this experiment was Merlinoite. A series of experiments was done to test the ability of synthesized zeolite as slow release potash and concluded that it proved to be potential fertilizer in agriculture [93]. A ball milled technique was used to synthesize the nano-fertilizer of dimensions 90-110nm using natural source of zeolite (Clinoptilolite). Zeolite was loaded with $ZnSO_4$. Experimental results revealed that release of Zn from nano-fertilizer substrate shows a prolonged period of 1176h where as zinc sulphate can retain Zn upto 216h only indicating that zinc nano-fertilizer can be used to improve the efficiency of crops to retain zinc for prolonged duration [94]. Zeolitic source used was clinoptilolite and modified it with Hexadecyltrimethyl ammonium to alter the charge on surface of clinoptilolite (negative to positive) to attract negatively charged ions in the substrate. The surface modified zeolite (SMZ) was then tested on Orthosiphonstamineous (in peat substrate on its growth). Modified zeolite on adding in peat substrate increases the availability of nutrients to the plant under study. It was observed in leachate experiments that when 20% of modified zeolite was added to substrate, the leaching of phosphate and nitrate reduces significantly [considered to be the potential substrate replacement to propagating substrate which is commercially available]. SMZ also allows the highest uptake of phosphate and nitrate ions, results in fast development and growth of plant [95]. AmbreenLateef et al. assessed the compatibility of using zeolite based nano-fertilizer as a supporting material for slow release of nine primary, secondary and micronutrients. Zeolitewas prepared by using sodium silicate solution (220g/300mL of distilled water) and ethylene glycol. They synthesized nano- composite by loading nutrients on nano-zeolite (NZ). Experimental data revealed that NZ releases nutrients slowly and also aids in germination, growth and flowering which proved that NZ can be used safely as eco-friendly fertilizer [96]. This study focused on development of valuable products (like eco friendly fertilizer) from the agricultural waste such as corncob. Nano-composite was developed using biochar of corncob.

This nano-composite is very cost effective and helps to increase yield of crop production and also decreases the environmental issues of other fertilizers. It also balances the carbon, pH, and improves water retaining capacity and ion exchange ability. Results explored that nano-composite can act as slow release and eco-friendly fertilizer [97]. AlpanaDubey et al. coated zeolite (commercial grade zeolite from India) with urea and used five different binders viz corn starch, potato starch, Bentonite clay, white cement and acryl polymer to develop a controlled release fertilizer which would be of low cost and also with inherent ion exchange capacity which helps to control the rate of release of nutrients from soil. The urea coated zeolite with acryl polymer binder (UZ-AP) observed to be most stable one. Studies revealed that UZ-AP has pore size of 135-150 micro meter with dense coating and controls N release by 55% [98]. Field study was carried out to know the exact effect of zeolite containing fertilizer (Zeotech N) in decreasing the leaching of nutrients in sodded turf grass. A seed mixture (70% Loliumperenne +30% Poapratensis) were sodded in eighteen established plots(containing substrate with v/v 20% peat) in the month of April in 2008.

This study was carried out to compare Zeotech N with mixture of conventional fertilizers. This experiment was conducted in two phases viz 1) Zeotech N and conventional fertilizer were used as 0, 25 and 50kg ha^{-1} N monthly and 0, 300 and 600 kg ha^{-1}N annually on 30th April, 28th May and 25th June 2008 respectively. 2) on 30th July, 27th August, 24th September 2008, the above mentioned fertilizer mixture was applied at the rate 0, 50 and 100 kg ha^{-1} N. Height and color of turf grass was observed per week by measuring the growth(vertical) and visual rating respectively and concluded that rate of increase of fertilization increases positively growth and color of turf grass. Results also showed that substrate with rate of fertilization 100kg ha^{-1} N monthly have high K and NO_3-N concentrations [99]. This study focused on the investigation of effect of zeolite (clinoptilolite and vermiculite) on three different parameters viz a) N and P acquiring enzyme activity, b) potential nitrification rate(PNR), c) availability of inorganic N(critical parameters for mineralization of Nitrogen).A mixture of clinoptilolite and vermiculite with urea was added to the agricultural soil (this experiment was conducted upto 60days). In addition to nitrogen supply, mix zeolite arrests activity of urease. Clinoptilolite influences the NH^{4+} and vermiculite retards the accumulation of nitrate in agricultural soil [100]. Qi Wu[1] along with others conducted an experiment on rice, and applied urea as nitrogen source at the rate 157.5 kg ha^{-1} (applied once or 3-way split with or without 10 t ha^{-1} zeolite) to evaluate its effect on production, N adsorption, properties of soil and morphology of roots in the year 2014 and 2015.

The results of this experiment showed that zeolite increased biomass, area of leaf and nitrogen adsorption, higher cation exchange capacity and availability of potassium in the growth period of plant under study. Nitrogen addition with zeolite can increase the yield of rice significantly by 9 or 11% as compared to nitrogen addition without zeolite [101]. The purpose of this study was to explore the ability of biochar to increase the rice production and retention of N in rice fields. In this experiment they coated biochar with Bentonite, starch and humic acid in combination as 25% biochar, 4% Bentonite and 10% humic acid with corn starch as adhesive. The synthesized product decreased leaching of nitrogen, water runoff loss at the stages of seedling and tillering as well as supplied maximum nutrients at maturing and heading stages of rice. The conclusion of this result was that bio-char based slow release fertilizer is efficient alternate to conventional nitrogen fertilizer for cultivation of rice [102].

Natural kaolinite and diatomite was used to synthesize the zeolite loaded with geopolymer (Z/G) to enhance the adsorption of PO_4^{3-} and NH_4^+ ions. S/G has sequestration capacities (Pseudo-second order kinetics) for phosphate and ammonium ions as 206 mg/g and 140 mg/g respectively. Sequestration reaction shows Langmuir behavior for adsorption.

Chemical complexation and ion exchange of Z/G involves the Gaussian energies of 12.4kJ/mol for phosphate and 10.47 kJ/mol for ammonium ions [103]. PerumalPalanivell and team synthesized immense pool of negatively charged ions by loading clinoptilolite zeolite with nitrogen, phosphorus and potassium fertilizers for retention and controlled release of nutrients for crop production. Five experimental set ups were used viz. 1)soil (250g) without zeolite. 2) Only 20g of zeolite 3) 20g zeolite with 250g soil.4) 40g zeolite with 250g soil 5) 60g zeolite with 250g soil. They concluded that clinoptilolite increased adsorption of nitrogen and phosphorus, desorption of nitrogen, pH of soil, availability and retention of NPK in soil and effectively decreased the water and soil pollution [104]. The experiment was conducted on peanut bean grown in sandy soil at Baloza Research Station of the Desert Research Center North Sinai, Egypt, in order to study the influence of application of 50, 75 and 100% rates of nano-zeolite phosphorus, zeolite phosphorus and superphosphate fertilizer to content of nutrients, adsorption by straw, peanut seeds crop and availability of nutrients in sandy soil. The dimensions of zeolite and nano-porous zeolite are 730.8 and 90.2nm respectively. Use of nano- zeolite in sandy soils resulted in maximum content of production having 1.2, 3.5, 1.47 ton fed^{-1} and 53% for pod, straw, crop and content of oil respectively. They concluded from this observation that nano-fertilizer usage results in the enhancement of nutrient adsorption [105]. V. B. Pandit et al. conducted the pot culture experiment during wet season in order to evaluate the influence of N and zeolite on concentration of nutrients and NUE (nitrogen use efficiency) in Oryzasativa in greenhouse conditions. As the levels of zeolite and N were increased, NPK concentrations and NUE also increased with 120kg N ha^{-1} and 9t ha^{-1} zeolite. Maximum recovery of N was 78% achieved by the usage of 120kg Nha^{-1} and 9t ha^{-1} [106].

This study focused on the effect of co-application of fertilizers, rice straw compost and clinoptilolite on NH_4^+ sorption, uptake of NPK nutrients and yield of maize (cobs). Experiment was conducted back to back for two planting cycles of maize form April-August (2014). Due to the sorption of ammonium on sites of exchange of straw and zeolite, mixed urea with straw and zeolite increased the NUE in corn cob in turn results in the high yield of corn cob and also increases the nutrient availability to soil [107]. JunlinZheng et al studied the enhancement of phosphorus uptake and availability in soil by addition of zeolite. They conducted this experiment with split plot design for two years to investigate the effect of zeolite on H_2O use, uptake of phosphorus and yield of rice under two different irrigation systems as improved alternate wetting and drying irrigation (IAWD) and continuous flooding irrigation (CF). IAWD reduced H_2O use and uptake of P and enhanced water-use efficiency (WUE) more effectively as compared to CF. Zeolite induced high crop yield is directly connected to increased uptake of phosphorus.

The application of zeolite increased retention of ammonium in upper layers of soil and also results in the prevention of nitrate leaching [108]. Experiment was performed for two consecutive years(2013 & 2014) to understand and investigate the role of natural nano- fertilizer loaded with nitrogen and bio-fertilizer (HNB) on crop yield, anatomy of leaf and seed, hormones, pigments of plants, carbohydrate content, fatty acids and oil content in Carumcarvi L. plant. Results revealed that HNB treatment increased growth rate, gross income and minimized cost of production [109]. Particle size of natural zeolite clinoptilolite was manipulated to micro level to study the sorption of phosphorus. Various adsorption experiments (Batch) were performed with 1g clinoptilolite +20mL of solution containing 0- 50mg of phosphorus per liter in background solution of 0.01M $CaCl_2$. 0.5M solution of sodium bicarbonate was used to measure desorption of P at pH 8.5. Studies on sorption were carried out at 5, 25 mg L^{-1} for 5,10,20,30 min; for 1, 2, 4, 8, 16 and 24h. Rota zeolite proved to be better sorption substrate than Gordes zeolite. Results indicated that sorption of P depends on particle size [110]. The aim of this investigation was to synthesize nano-zeolite (NZ) using rice husk with aluminum foils by calcinations and zeolitization process. NZ have high cation exchange capacity and a better substrate for bacterial cells responsible for nitrogen fixation and solubilization of phosphorus, a hydro-cracking material and also increased the fertility of soil results in better growth of plant especially in arid zones [111].

Natural zeolite (clinoptilolite) from Mehran mining company Pakistan first sieved from 0.250mm sieve and then examined for cation exchange capacity. Various experiments viz. T_0-control, T_1- urea fertilizer, T_2- zeo-urea(1:1), T_3-zeo-urea (2:1), T_4- zeo-urea (3:1), T_5-zeo-urea (1:2), and T_6- zeo-urea (1:3) were carried out to reduce the nitrogen loss as NH_4-N, NO_3-N leaching and volatilization of ammonia from agricultural soils. After the treatment of fertilizers and control, leaching was done at 4, 8, 12, 19, 25, 39 and 45 days and volatilization of ammonia was analyzed at 1,5,9,13 and 20 days. The leachate samples were collected and examined and they observed that the zeolitic fertilizer reduces the nitrogen loss as NH_4-N by 13% in Alfisol soils and 28% in Spodosol soils by 1:1 zeo-urea, and NO_3-N by 3:1 zeo-urea in Alfisol soils. 1:1 zeo-urea also reduces the ammonia volatilization by 47% and 32% in Spodosol and Alfisol soils respectively.

These results indicated that 1:1 zeo-urea can be used as best alternative to conventional fertilizers for reduction of nitrogen loss [112]. Research was performed to evaluate the capability of Bentonite and natural zeolite (1:10 ratio), for changing the chemical and physical properties, and few parameters of growth and production of yield of Zea maize and Viciafaba L. under two different irrigation systems- drip irrigation system and natural drainage. At the rate 0, 1.5, 2 and 2.5 ton/fed addition of soil conditioner were done. Increasing application rate of soil conditioner, directly affects the physical properties of soil. Sandy soil can be converted to loamy sand by increasing the clay content. These observation results revealed that application of natural zeolite and Bentonite in high magnitude improves the soil properties from sandy to loamy [113]. The aim of this study was to evaluate the use of cattle slurry (digested anareobically) mixed with natural zeolite for the production of rapeseed. Plant under study was “Bristol” and a comparison of cattle slurry fertilizer with conventional fertilizer was done for the cultivation of rapeseed. Improved quality of cattle slurry with zeolite as bulking agent were applied to soil and observed to be beneficial for end product. Experimental data explored that the addition of clinoptilolite with cattle slurry enhanced the growth of plant and yield content of rapeseed [114]. T.Campisi et al. studied the ammonium charged Chabazite to reduce the nitrate leaching from soil and increase the corn production. For the observation of growth and characteristics of maize forty-eight lysimeters of zeolite: soil in two trials was used in greenhouse. Leaching concentration of nitrate under different conditions of fertilization (standard, high or 70%, medium or 50% and 30% of fertilization rate) and treatment of ammonium charged zeolite (control, 0, 1.5 t ha^{-1}, 2, 100 t ha^{-1}) [115].

Zhiwu Lei et al. modified kaolinite with H_3PO_4 (by grinding) to increase the fixation of potassium by introducing more protons (H^+) ions for K exchange. They also synthesized layered double hydroxides (LDH) by milling magnesium and aluminum hydroxides used for incorporation of nitrate anions. Exchanged action of OH^{-1} from LDH with K^+cations- allows high efficiency to achieve desalination of salts of alkali metal and recovery of K from various waste materials and serves as slow release fertilizer for potassium [116]. This research work focused on the study of nitrogen absorption and slow release ability of natural zeolite clinoptilolite from anareobically digested livestock manure (Digestate). Experiment was carried out on strawberry plant. They studied the effects of added zeolite on plant growth, quality of fruit, and abundance of prokaryotic nitrifying bacteria. Results confirmed that mixture of natural zeolite with Digestate showed improved plant growth and fruit quality and also act as the efficient nitrogen absorber and slow release fertilizer [117]. M. Yuvaraj and K. S. Subramanian synthesized a zinc controlled release fertilizer using clinoptilolite loaded with zinc sulphate.

Nano dimension (90- 110nm) zeolite was achieved by ball milling technique andthen loaded it with zinc sulphate. Results showed that zinc release from the synthesized zeolite has long period of 1176h as compared to the conventional Zn fertilizer which showed a releasing period of 216h. These results indicated that zeolite zinc fertilizer can improve the soil efficiency for crops by increasing the zinc retaining ability of soil [118]. PiseyHoeung et al. developed a slow release urea-zeolite fertilizer to increase the efficiency of urea fertilizer. In the process of granulation, particles of urea and zeolite in the mixture of 50, 60 and 80 mesh were used with solution of starch (2% to 10%) and clay (5%, 7.5% and 10%) as binders. Results showed that 3-4 mm granule size, 60-mesh particle size of urea-zeolite, 7.5% clay, 3% starch were considered to be the best condition for slow release rate. They concluded that the prepared zeolite fertilizer will show the release period of three months, particularly for rice [119]. This work investigated the properties of Brazilian zeolitic material as slow nutrient release fertilizer and soil conditioner. A head sample was prepared stilbite zeolite, smectic clay and quartz. Natural zeolite was enriched with NPK by the addition of KNO_3, K_2HPO_4 and H_3PO $^+$.

The test was carried out on four successive crops viz lettuce, tomato, rice and Andropogon grass. The test results revealed that zeolite loaded with NPK not only proved to be a controlled release fertilizer of nutrients but also increased the yield of crop by 20% [120]. A. Manikandan and K. S. Subramanian developed a nano-fertilizer in order to deliver nutrients in a regulated manner to plants. They used the natural source of zeolite clinoptiloliteand loaded it with urea to synthesize the novel nano-fertilizer. The effect of this modified zeolite was tested on maize plant grown in Alfisols and Inceptisol soils. The nanozeoureaeffects more on Inceptisol soils and retains more nitrogen as compared to Alfisol [121]. This paper focused on the study of the influence of potassium hydroxide concentration and time of crystallization on the zeolite synthesis and its slow release behavior. They observed that zeolite-F is stable under higher concentration of KOH(4-5 mol kg^{-1}) under temperature of 95° C. Various tests like water solute release tests were conducted to check its efficiency as slow release fertilizer for K_2O. Zeolite-F has pore size of 0.513nm and 27m^2/g of surface area [122]. Dina kartikaMaharam along with others used zeolite and chitosan composites as controlled release fertilizer. A fertilizer was synthesized by mixing zeolite with sodium nitrate (as nitrogen source) and chitosan was used as cross-linker.

Modification of zeolite was done by incorporating zeolite with sodium nitrate and solution of chitosan [123].

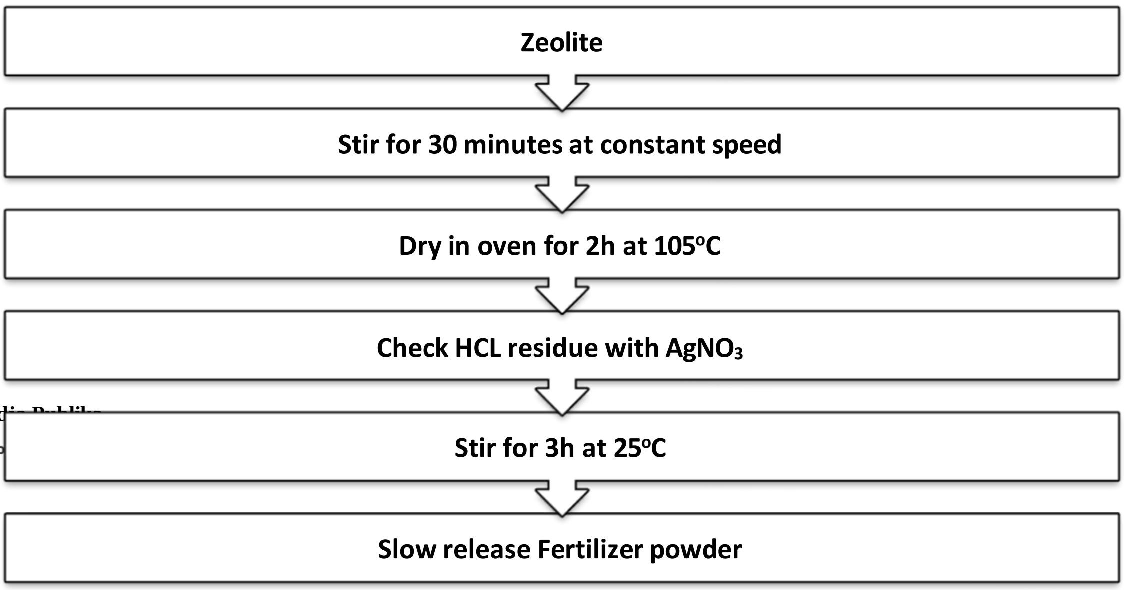
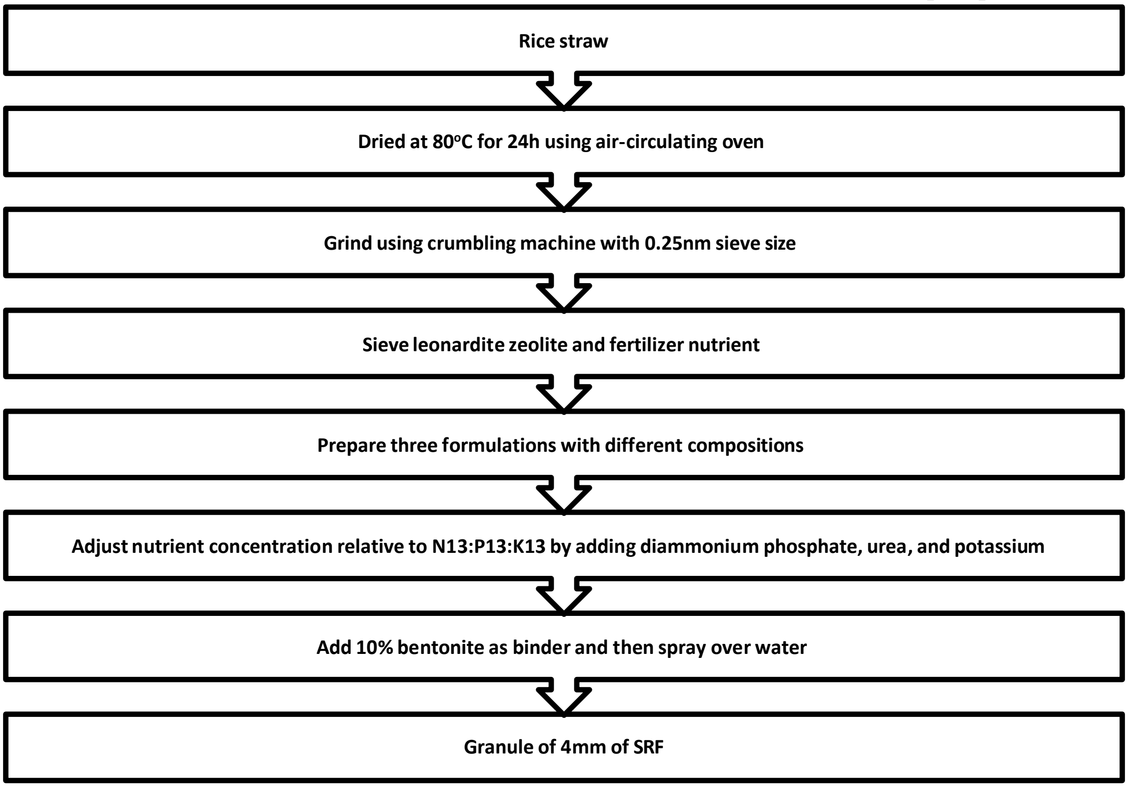
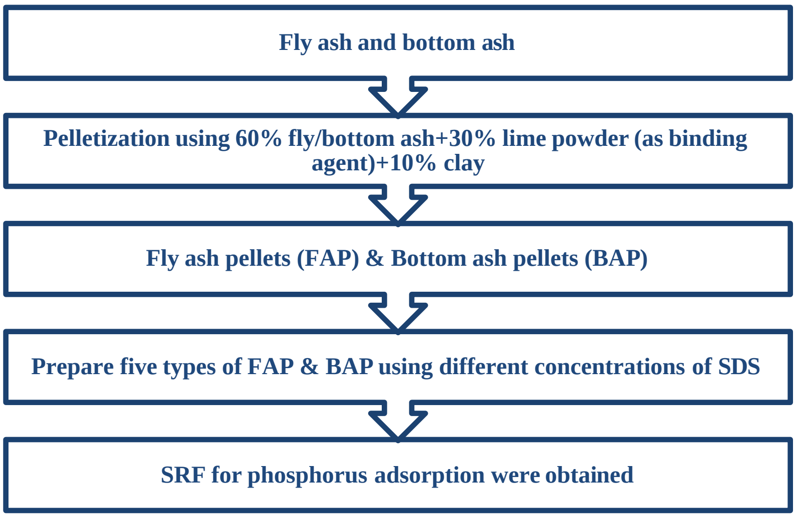


Fig.1.4. Diagrammatic Representation of synthesis of slow release fertilizer.

This study was mainly about the slow release nature of three waste materials viz. leonardite, zeolite and rice straw. They used different compositions of above said three waste materials to form four different types of slow release fertilizer for NPK nutrients. Concentration of nutrients in each type of synthesized slow release material was adjusted in accordance to relate to N13; P13;K13 commercially available SRF. The binder used so in this synthesis process was bentonite. Resin was used to coat each newly synthesized four formulations. Experimental studies showed that coated zeolite acts as better slow release fertilizer that uncoated one [124].



PiseyHoeung et al. modified the zeolite to enhance the effectiveness and functionality of urea fertilizer. The main motive of this study was to synthesize a granular slow release fertilizer. They used natural zeolite, urea, and solution of binder for granulation. In order to determine the rate of slow release of urea from synthesized granular zeolite percolation reactor was used. Experimental results determined that 3-4mm granular size, particle size of 60 mesh of urea- zeolite, 7.5% of clay, 3% starch binder was considered as best for synthesis of slow release fertilizer, texture of granule and is highly cost effective [125]. This study was mainly about the recycling of solids obtained from combustion of coal which are very hazardous to environment. They synthesized a pelletized-adsorbent for dissolved phosphorus. Coal fly ash pellets (FAP) and bottom ash pellets (BAP) were modified using ionic surfactant sodium dodecyl sulfate (SDS) to increase the phosphorus adsorption capacity of FAP and BAP. They synthesized 10 kinds of FAP and BAP using different concentrations of FAP, BAP and SDS at higher temperature of 700°C. The SDS addition results in the increase in porosity of FAP and BAP as 46-164%, 53-77% respectively. Synthesized modified pellets were used in field edges and in- stream to decrease the leaching of phosphorus from crop lands [126].



RadhaTomar et al focused on usage of nano-particles of clinoptilolite and montnorilloniteand their modified forms for slow release of phosphate. In order to determine the effect of different parameters viz. concentration of phosphate, medium pH, time of contact between adsorbent and adsorbate, adsorbent weight and temperature various batch experiments were used. These studies determined that the modified forms show better adsorption capacity as compared to unmodified one and also revealed that pH 7 is considered to be the best for maximum adsorption of phosphate [127].

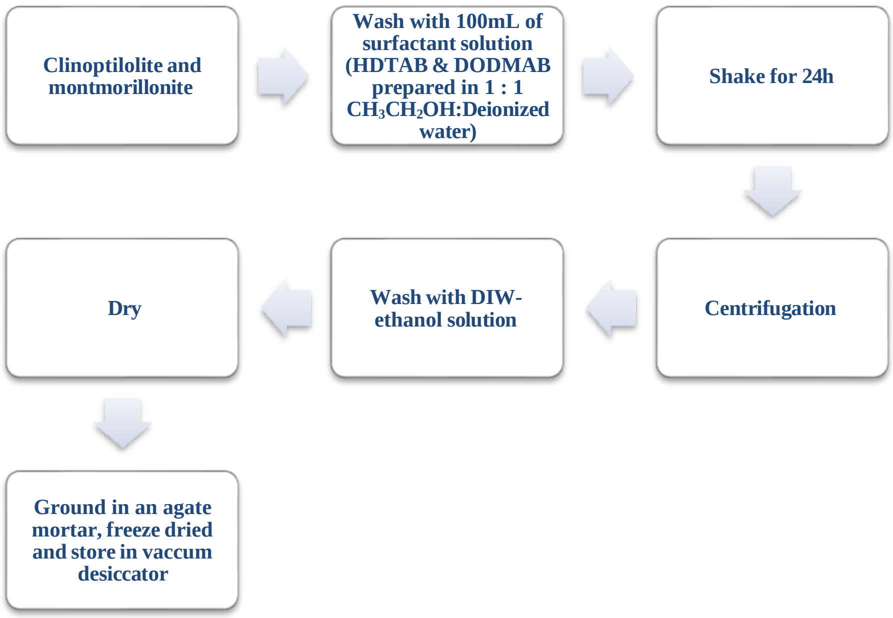


Fig.1.5 Flow chart for the synthesis of surfactant modified Zeolite

The ultimate fertilizer should be inexpensive and long lasting, should tend to increase soil fertility through repeated use and should release nutrients to plants as they are needed, thereby eliminating pollution and inefficiencies. The use of soluble fertilizers can lead to water pollution and to wasted nutrients. Nitrogen, for example, can leach into the ground and surface waters especially in sandy soils and phosphate may become fixed and unavailable to plants especially in tropical soils. Surfactant modified zeolites is used to reduce the leaching of plant nutrients and as support for the slow release formulations of fertilizers. The slow release and reduced leaching enable the attaining of relatively larger and consistent fertilizer concentration in the root zone for relatively longer periods. Hence the new materials are advantageous from both the economical and the environmental point of view.

Conclusion

Up to now , improving the ability of the fertilizers is an important task for agriculture to increase and improve the fertility, physical and chemical properties of soil. Use of fertilizers at alarming and uncontrolled rate leads to environmental pollution. The study of current literature sources shows that the use of surface modified zeolites as a prolonged fertilizer has a positive effect on nutrition of plants, prevents leaching, and promotes slow release of nutritients into the soil. Applications of surface modified zeolites as fertilizers produces positive impact in all types of soils and increases the production of crops. Due to the special crystalline structure, zeolites have excellent adsorption, ion exchange capacity and good catalytic properties. Surface modification ehances these abilities of zeolites and make them more suitable and fit for all types of soils and prevents leaching of nutrients more effectively and makes them less harmful to the environment.

Referances

1. Vogt, E. T., Whiting, G. T., Chowdhury, A. D., &Weckhuysen, B. M. (2015). Zeolites and zeotypes for oil and gas conversion. In *Advances in catalysis* (Vol. 58, pp. 143- 314). Academic Press.
2. Gaidoumi, A. E., Benabdallah, A. C., Bali, B. E., &Kherbeche, A. (2018). Synthesis and characterization of zeolite HS using natural pyrophyllite as new clay source. *Arabian Journal for Science and Engineering*, *43*(1), 191-197.
3. Moshoeshoe, M., Nadiye-Tabbiruka, M. S., &Obuseng, V. (2017). A review of the chemistry, structure, properties and applications of zeolites. *Am. J. Mater. Sci*, *7*(5), 196-221.
4. Ekpe, Ikenna. (2017). Zeolite Synthesis, Characterisation and Application Areas: A Review. *International Research Journal of Environmental Sciences*. 6.
5. Yilmaz, B., Trukhan, N., &MüLLER, U. (2012). Industrial outlook on zeolites and metal organic frameworks. *Chinese Journal of Catalysis*, *33*(1), 3-10.
6. Armbruster, T., & Gunter, M. E. (2001). Crystal structures of natural zeolites. *Reviews in mineralogy and geochemistry*, *45*(1), 1-67.
7. Petrov, I., &Michalev, T. (2012). Synthesis of zeolite A: a review. *Научнитрудовенарусенскияуниверситет*, *51*, 30-35.
8. Widiastuti, N., Wu, H., Ang, H. M., & Zhang, D. (2011). Removal of ammonium from greywater using natural zeolite. *Desalination*, *277*(1-3), 15-23.
9. Valdés, M. G., Perez-Cordoves, A. I., & Diaz-Garcia, M. E. (2006). Zeolites and zeolite-based materials in analytical chemistry. *TrAC Trends in Analytical Chemistry*, *25*(1), 24-30.
10. Bacakova, L., Vandrovcova, M., Kopova, I., &Jirka, I. (2018). Applications of zeolites in biotechnology and medicine–a review. *Biomaterials science*, *6*(5), 974-989.
11. Derbe, T., Temesgen, S., &Bitew, M. (2021). A Short Review on Synthesis, Characterization, and Applications of Zeolites. *Advances in Materials Science & Engineering*.
12. Xu, R., Pang, W., Yu, J., Huo, Q., & Chen, J. (2009). *Chemistry of zeolites and related porous materials: synthesis and structure*. John Wiley & Sons.
13. Deng, L., Xu, Q., & Wu, H. (2016). Synthesis of zeolite-like material by hydrothermal and fusion methods using municipal solid waste fly ash. *Procedia Environmental Sciences*, *31*, 662-667.
14. Wang, Cheng & Shi, Huisheng& Li, Yan. (2012). Synthesis and characterization of natural zeolite supported Cr-doped TiO2 photocatalysts. Applied Surface Science. 258. 4328–4333. 10.1016/j.apsusc.2011.12.108
15. Holmberg, Brett & Wang, Huanting&Norbeck, Joseph & Yan, Yushan. (2003). Controlling size and yield of zeolite Y nanocrystals using tetramethylammonium bromide. Microporous and Mesoporous Materials. 59. 13-28. 10.1016/S1387- 1811(03)00271-3
16. Thompson, R. W. (1998). Recent advances in the understanding of zeolite synthesis. *Synthesis*, 1-33.
17. Kianfar, E. (2019). Nanozeolites: synthesized, properties, applications. *Journal of Sol- Gel Science and Technology*, *91*(2), 415-429.
18. Wang, Z., Mitra, A., Wang, H., Huang, L., & Yan, Y. (2001). Pure Silica Zeolite Films as Low-k Dielectrics by Spin-On of Nanoparticle Suspensions. *Advanced Materials*, *13*, 1463-1466.
19. Tang, Ting & Zhang, Lei & Dong, Hai& Fang, Zhongxue& Fu, Wenqian& Yu, Quanyong& Tang, Tiandi. (2017). Organic template-free synthesis of zeolite Y nanoparticle assemblies and their application in the catalysis of the Ritter reaction. RSC Adv.. 7. 7711-7717. 10.1039/C6RA27129D.
20. Huang, Y., Wang, K., Dong, D., Li, D., Hill, M. R., Hill, A. J., & Wang, H. (2010). Synthesis of hierarchical porous zeolite NaY particles with controllable particle sizes. *Microporous and*

Mesoporous Materials, *127*(3), 167-175.

21. Yang, N., Yue, M., & Wang, Y. (2012). Synthesis of zeolites by dry gel conversion. *Progress in Chemistry*, *24*(0203), 253.
22. Zhou, D., Lu, X., Xu, J., Yu, A., Li, J., Deng, F., & Xia, Q. (2012). Dry gel conversion method for the synthesis of organic–inorganic hybrid MOR zeolites with modifiable catalytic activities. *Chemistry of Materials*, *24*(21), 4160-4165.
23. Weitkamp, J., & Hunger, M. (2005). Preparation of zeolites via the dry-gel synthesis method. In *Studies in Surface Science and Catalysis* (Vol. 155, pp. 1-12). Elsevier.
24. Jain, R., &Rimer, J. D. (2020). Seed-Assisted zeolite synthesis: The impact of seeding conditions and interzeolite transformations on crystal structure and morphology. *Microporous and Mesoporous Materials*, *300*, 110174.
25. Sousa, L. V., Silva, A. O., Silva, B. J., Teixeira, C. M., Arcanjo, A. P., Frety, R., & Pacheco, J. G. (2017). Fast synthesis of ZSM-22 zeolite by the seed-assisted method of crystallization with methanol. *Microporous and Mesoporous Materials*, *254*, 192-200.
26. Imai, H., Hayashida, N., Yokoi, T., &Tatsumi, T. (2014). Direct crystallization of CHA-type zeolite from amorphous aluminosilicate gel by seed-assisted method in the absence of organic-structure-directing agents. *Microporous and mesoporous materials*, *196*, 341-348.
27. Zeng, X., Hu, X., Song, H., Xia, G., Shen, Z. Y., Yu, R., &Moskovits, M. (2021). Microwave synthesis of zeolites and their related applications. *Microporous and Mesoporous Materials*, *323*, 111262.
28. Li, Y., & Yang, W. (2008). Microwave synthesis of zeolite membranes: A review. *Journal of Membrane Science*, *316*(1-2), 3-17.
29. Makgabutlane, B., Nthunya, L. N., Nxumalo, E. N., Musyoka, N. M., & Mhlanga, S. D. (2020). Microwave irradiation-assisted synthesis of zeolites from coal fly ash: An optimization study for a sustainable and efficient production process. *ACS omega*, *5*(39), 25000-25008.
30. Srilai, S., Tanwongwan, W., Onpecth, K., Wongkitikun, T., Panpiemrasda, K., Panomsuwan, G., &Eiad-ua, A. (2020, October). Synthesis of zeolite A from bentonite via hydrothermal method: The case of different base solution. In *AIP Conference Proceedings* (Vol. 2279, No. 1, p. 060006). AIP Publishing LLC.
31. Nyankson, E., Efavi, J. K., Yaya, A., Manu, G., Asare, K., Daafuor, J., &Abrokwah, R. Y. (2018). Synthesis and characterisation of zeolite-A and Zn-exchanged zeolite-A based on natural aluminosilicates and their potential applications. *Cogent Engineering*, *5*(1), 1440480.
32. Khan, G. M., Arafat, S. M. Y., Reza, M. N., Razzaque, S. M., &Alam, M. (2010). Linde Type-A zeolite synthesis and effect of crystallization on its surface acidity.
33. Parnham, E. R., & Morris, R. E. (2007). Ionothermal synthesis of zeolites, metal– organic frameworks, and inorganic–organic hybrids. *Accounts of chemical research*, *40*(10), 1005-1013.
34. Wang, Y., Xu, Y., Li, D., Liu, H., Li, X., Tao, S., &Tian, Z. (2015). Ionothermal synthesis of zeoliticimidazolate frameworks and the synthesis dissolution- crystallization mechanism. *Chinese Journal of Catalysis*, *36*(6), 855-865.
35. Naber, J. E., De Jong, K. P., Stork, W. H. J., Kuipers, H. P. C. E., & Post, M. F. M. (1994). Industrial applications of zeolite catalysis. In *Studies in surface science and catalysis* (Vol. 84, pp. 2197-2219). Elsevier.
36. Primo, A., & Garcia, H. (2014). Zeolites as catalysts in oil refining. *Chemical Society Reviews*, *43*(22), 7548-7561.
37. Yilmaz, B., & Müller, U. (2009). Catalytic applications of zeolites in chemical industry. *Topics in Catalysis*, *52*(6), 888-895.
38. Martin, A. (2016). Zeolite catalysis. *Catalysts*, *6*(8), 118.
39. Zou, H., Sun, Q., Fan, D., Fu, W., Liu, L., & Wang, R. (2015). Facile synthesis of yolk/core-shell structured TS-1@ mesosilica composites for enhanced hydroxylation of phenol. *Catalysts*, *5*(4), 2134-2146.
40. Gliozzi, G., Passeri, S., Bortolani, F., Ardizzi, M., Mangifesta, P., &Cavani, F. (2015). Zeolite catalysts for phenol benzoylation with benzoic acid: Exploring the synthesis of hydroxybenzophenones. *Catalysts*, *5*(4), 2223-2243.
41. Wang, Y., Yokoi, T., Namba, S., &Tatsumi, T. (2016). Effects of dealumination and desilication of beta zeolite on catalytic performance in n-hexane cracking. *Catalysts*, *6*(1), 8.
42. Han, J., Jiang, G., Han, S., Liu, J., Zhang, Y., Liu, Y., ...& Wei, Y. (2016). The fabrication of

Ga2O3/ZSM-5 hollow fibers for efficient catalytic conversion of n- butane into light olefins and aromatics. *Catalysts*, *6*(1), 13.

43. Liu, G., Zhao, Y., &Guo, J. (2016). High selectively catalytic conversion of lignin- based phenols into para-/m-xylene over Pt/HZSM-5. *Catalysts*, *6*(2), 19.
44. Fattahi, N., Triantafyllidis, K., Luque, R., &Ramazani, A. (2019). Zeolite-based catalysts: a valuable approach toward ester bond formation. *Catalysts*, *9*(9), 758.
45. Liu, L., &Corma, A. (2020). Evolution of isolated atoms and clusters in catalysis. *Trends in Chemistry*, *2*(4), 383-400.
46. Pandiangan, K. D., Simanjuntak, W., Pratiwi, E., &Rilyanti, M. (2019, October). Characteristics and catalytic activity of zeolite-a synthesized from rice husk silica and aluminium metal by sol-gel method. In *Journal of Physics: Conference Series* (Vol. 1338, No. 1, p. 012015). IOP Publishing.
47. Reiprich, B., Tarach, K. A., Pyra, K., Grzybek, G., &Góra-Marek, K. (2022). High- Silica Layer-like Zeolites Y from Seeding-Free Synthesis and Their Catalytic Performance in Low-Density Polyethylene Cracking. *ACS applied materials & interfaces*, *14*(5), 6667-6679.
48. Dragomirova, R., &Wohlrab, S. (2015). Zeolite membranes in catalysis—From separate units to particle coatings. *Catalysts*, *5*(4), 2161-2222.
49. Li, Y., Li, L., & Yu, J. (2017). Applications of zeolites in sustainable chemistry. *Chem*, *3*(6), 928-949.
50. Pan, T., Wu, Z., & Yip, A. C. (2019). Advances in the green synthesis of microporous and hierarchical zeolites: a short review. *Catalysts*, *9*(3), 274.
51. Margeta, K., Logar, N. Z., Šiljeg, M., &Farkaš, A. (2013). Natural zeolites in water treatment–how effective is their use. *Water treatment*, *5*, 81-112.
52. Koshy, N., & Singh, D. N. (2016). Fly ash zeolites for water treatment applications. *Journal of Environmental Chemical Engineering*, *4*(2), 1460-1472.
53. Rahman, M. M., Hasnida, N., &Nik, W. W. (2009). Preparation of zeolite Y using local raw material rice husk as a silica source. *Journal of Scientific Research*, *1*(2), 285-291.
54. Gadhban, M. Y., Abdulmajed, Y. R., Ali, F. D., & Al-Sharify, Z. T. (2020, June). Preparation of Nano Zeolite and itsApplication in Water Treatment. In *IOP Conference Series: Materials Science and Engineering* (Vol. 870, No. 1, p. 012054). IOP Publishing.
55. Jiang, N., Shang, R., Heijman, S. G., &Rietveld, L. C. (2018). High-silica zeolites for adsorption of organic micro-pollutants in water treatment: A review. *Water research*, *144*, 145-161.
56. Nazarenko, O., &Zarubina, R. (2013). Application of sakhaptinsk zeolite for improving the quality of ground water. *Energy and Environmental Engineering*, *1*(2), 68-73.
57. Itskos, G., Koutsianos, A., Koukouzas, N., &Vasilatos, C. (2015). Zeolite development from fly ash and utilization in lignite mine-water treatment. *International journal of mineral processing*, *139*, 43-50.
58. Azamat, J., &Khataee, A. (2017). Improving the performance of heavy metal separation from water using MoS2 membrane: molecular dynamics simulation. *Computational Materials Science*, *137*, 201-207.
59. Motsa, M. M., Msagati, T. A. M., Thwala, J. M., & Mamba, B. B. (2015). Polypropylene–zeolite polymer composites for water purification: synthesis, characterisation and application. *Desalination and Water Treatment*, *53*(10), 2604- 2612.
60. Chen, X., Yu, L., Zou, S., Xiao, L., & Fan, J. (2020). Zeolite cotton in tube: A simple robust household water treatment filter for heavy metal removal. *Scientific Reports*, *10*(1), 1-9.
61. Haralambous, A., Maliou, E., &Malamis, M. (1992). The use of zeolite for ammonium uptake. *Water Science and Technology*, *25*(1), 139-145.
62. Kadhom, M., & Deng, B. (2018). Metal-organic frameworks (MOFs) in water filtration membranes for desalination and other applications. *Applied Materials Today*, *11*, 219- 230.
63. Paragas, D. S., Salazar, J. R., &Ginez, M. O. (2014). Preparation, Characterization and Application of Rice hull-derived zeolites in water treatment. *Journal of Asian Scientific Research*, *4*(7), 348-355.
64. Ippolito, J. A., Tarkalson, D. D., &Lehrsch, G. A. (2011). Zeolite soil application method affects inorganic nitrogen, moisture, and corn growth. *Soil science*, *176*(3), 136-142.
65. Mumpton, F. A. (1999). La rocamagica: Uses of natural zeolites in agriculture and industry. *Proceedings of the National Academy of Sciences*, *96*(7), 3463-3470.
66. Nakhli, S. A. A., Delkash, M., Bakhshayesh, B. E., &Kazemian, H. (2017). Application of zeolites for sustainable agriculture: a review on water and nutrient retention. *Water, Air, & Soil Pollution*, *228*(12), 1-34.

67. De Smedt, C., Someus, E., &Spanoghe, P. (2015). Potential and actual uses of zeolites in crop protection. *Pest management science*, *71*(10), 1355-1367.
68. Ahmed, O. H., Sumalatha, G., &Muhamad, A. N. (2010). Use of zeolite in maize (Zea mays) cultivation on nitrogen, potassium and phosphorus uptake and use efficiency. *International Journal of the Physical Sciences*, *5*(15), 2393-2401.
69. Gül, A., Eroğul, D., &Ongun, A. R. (2005). Comparison of the use of zeolite and perlite as substrate for crisp-head lettuce. *ScientiaHorticulturae*, *106*(4), 464-471.
70. de Campos Bernardi, A. C., Oliviera, P. P. A., de Melo Monte, M. B., & Souza-Barros, F. (2013). Brazilian sedimentary zeolite use in agriculture. *Microporous and Mesoporous Materials*, *167*, 16-21.
71. Torma, S., Vilcek, J., Adamisin, P., Huttmanova, E., &Hronec, O. (2014). Influence of natural zeolite on nitrogen dynamics in soil. *Turkish Journal of Agriculture and Forestry*, *38*(5), 739-744.
72. Boros-Lajszner, E., Wyszkowska, J., &Kucharski, J. (2018). Use of zeolite to neutralise nickel in a soil environment. *Environmental monitoring and assessment*, *190*(1), 1-13.
73. Noori, M., Zendehdel, M., &Ahmadi, A. (2006). Using natural zeolite for the improvement of soil salinity and crop yield. *Toxicological & Environmental Chemistry*, *88*(1), 77-84.
74. Baninasab, B. (2009). Effects of the application of natural zeolite on the growth and nutrient status of radish (Raphanussativus L.). *The Journal of Horticultural Science and Biotechnology*, *84*(1), 13-16.
75. Joughehdoust, S., &Manafi, S. (2008). Application of zeolite in biomedical engineering: a review. In *Proceedings of the Iran International Zeolite Conference (IIZC'08), Tehran*.
76. Vargas, A. M., Cipagauta-Ardila, C. C., Molina-Velasco, D. R., & Ríos-Reyes, C. A. (2020). Surfactant-modified natural zeolites as carriers for diclofenac sodium release: A preliminary feasibility study for pharmaceutical applications. *Materials Chemistry and Physics*, *256*, 123644.
77. Attia, T. M. S., & Hu, X. L. (2013). Synthesized magnetic nanoparticles coated zeolite for the adsorption of pharmaceutical compounds from aqueous solution using batch and column studies. *Chemosphere*, *93*(9), 2076-2085.
78. Bhardwaj, D., Sharma, M., Sharma, P., &Tomar, R. (2012). Synthesis and surfactant modification of clinoptilolite and montmorillonite for the removal of nitrate and preparation of slow release nitrogen fertilizer. *Journal of hazardous materials*, *227*, 292-300.
79. Zwingmann, N., Singh, B., Mackinnon, I. D., &Gilkes, R. J. (2009). Zeolite from alkali modified kaolin increases NH4+ retention by sandy soil: Column experiments. *Applied Clay Science*, *46*(1), 7-12.
80. Stamatakis, M. G., Stamataki, I. S., Giannatou, S., Vasilatos, C., Drakou, F., Mitsis, I., &Xinou, K. (2017). Characterization and evaluation of chabazite-and mordenite-rich tuffs, and their mixtures as soil amendments and slow release fertilizers. *Archives of Agronomy and Soil Science*, *63*(6), 735-747.
81. Perrin, T. S., Drost, D. T., Boettinger, J. L., & Norton, J. M. (1998). Ammonium-loaded clinoptilolite: a slow-release nitrogen fertilizer for sweet corn. *Journal of plant nutrition*, *21*(3), 515-530.
82. Rahmat, H., Ganjar, F., Uswatul, C., Sayekti, W., & Ari, H. R. (2015). Effectiveness of urea nanofertilizer based aminopropyltrimethoxysilane (APTMS)-zeolite as slow release fertilizer system. *African Journal of Agricultural Research*, *10*(14), 1785-1788.
83. Rajonee, A. A., Nigar, F., Ahmed, S., &Huq, S. I. (2016). Synthesis of nitrogen nano fertilizer and its efficacy. *Canadian Journal of Pure and Applied Sciences*, *10*, 3913- 3919.
84. Li, Z., Zhang, Y., & Li, Y. (2013). Zeolite as slow release fertilizer on spinach yields and quality in a greenhouse test. *Journal of Plant Nutrition*, *36*(10), 1496-1505.
85. Malekian, R., Abedi-Koupai, J., &Eslamian, S. S. (2011). Use of zeolite and surfactant modified zeolite as ion exchangers to control nitrate leaching. *International Journal of Geological and Environmental Engineering*, *5*(4), 267-271.
86. Bansiwal, A. K., Rayalu, S. S., Labhasetwar, N. K., Juwarkar, A. A., &Devotta, S. (2006). Surfactant-modified zeolite as a slow release fertilizer for phosphorus. *Journal of Agricultural and Food Chemistry*, *54*(13), 4773-4779.
87. Zhou, H., Bhattarai, R., Li, Y., Li, S., & Fan, Y. (2019). Utilization of coal fly and bottom ash pellet for phosphorus adsorption: Sustainable management and evaluation. *Resources, Conservation and Recycling*, *149*, 372-380.
88. Li, Z. (2003). Use of surfactant-modified zeolite as fertilizer carriers to control nitrate release. *Microporous and mesoporous materials*, *61*(1-3), 181-188.
89. Abdul Majid, S., Ahmad Mir, M., & Mir, J. M. (2018). Nitrate and phosphate sorption efficiency of

mordenite versus zeolite-A at the convergence of experimental and density functionalized evaluation. *Journal of the Chinese Advanced Materials Society*, *6*(4), 691-705.

90. Lin, K., Liu, P., Wei, L., Zou, Z., Zhang, W., Qian, Y., ...& Chang, J. (2013). Strontium substituted hydroxyapatite porous microspheres: surfactant-free hydrothermal synthesis, enhanced biological response and sustained drug release. *Chemical engineering journal*, *222*, 49-59.
91. Bhardwaj, D., Sharma, M., &Tomar,R.(2014). Removal and slow release studies of phosphate on surfactant loaded hydrothermally synthesized silicate nanoparticles. Journal of the Taiwan Institute of Chemical Engineers, 45(5), 2649-2658.
92. Manikandan, A., & Subramanian, K. S. (2014). Fabrication and characterisation of nanoporous zeolite based N fertilizer. *Afr J Agric Res*, *9*(2), 276-284.
93. MohdRusli, R. (2014). Leachate Pollutants Adsorption Using Potassium Hydroxide and Surfactant Modified Bentonite for Possible Use as Slow Release Fertiliser. *Iranian (Iranica) Journal of Energy & Environment*, *5*(3).
94. Flores, C. G., Schneider, H., Marcilio, N. R., Ferret, L., & Oliveira, J. C. P. (2017). Potassic zeolites from Brazilian coal ash for use as a fertilizer in agriculture. *Waste Management*, *70*, 263-271.
95. Yuvaraj, M., & Subramanian, K. S. (2018). Development of slow release Zn fertilizer using nano-zeolite as carrier. *Journal of plant nutrition*, *41*(3), 311-320.
96. Jie, L. Y., &Malek, N. A. N. N. (2018). Application of Surfactant-Modified Clinoptilolite in Peat Substrate on the Growth of Orthosiphonstamineus. *Communications in Soil Science and Plant Analysis*, *49*(19), 2465-2477.
97. Lateef, A., Nazir, R., Jamil, N., Alam, S., Shah, R., Khan, M. N., &Saleem, M. (2016). Synthesis and characterization of zeolite based nano–composite: An environment friendly slow release fertilizer. *Microporous and Mesoporous Materials*, *232*, 174-183.
98. Lateef, A., Nazir, R., Jamil, N., Alam, S., Shah, R., Khan, M. N., &Saleem, M. (2019). Synthesis and characterization of environmental friendly corncob biochar based nano- composite–A potential slow release nano-fertilizer for sustainable agriculture. *Environmental Nanotechnology, Monitoring & Management*, *11*, 100212.
99. Dubey, A., &Mailapalli, D. R. (2019). Zeolite coated urea fertilizer using different binders: Fabrication, material properties and nitrogen release studies. *Environmental Technology & Innovation*, *16*, 100452.
100. Macolino, S., &Zanin, G. (2014, August). Effectiveness of a zeolite-based fertilizer in reducing nutrient leaching in a recently sodded turfgrass. In *XXIX International Horticultural Congress on Horticulture: Sustaining Lives, Livelihoods and Landscapes (IHC2014): III 1122* (pp. 73-82).
101. Tzanakakis, V. A., Monokrousos, N., &Chatzistathis, T. (2021). Effects of clinoptilolite zeolite and vermiculite on nitrification and nitrogen and phosphorus acquiring enzymes in a nitrogen applied agricultural soil. *Journal of Soil Science and Plant Nutrition*, *21*(4), 2791-2802.
102. Wu, Q., Chen, T., Chi, D., Xia, G., Sun, Y., & Song, Y. (2019). Increasing nitrogen use efficiency with lower nitrogen application frequencies using zeolite in rice paddy fields. *International Agrophysics*, *33*(2).
103. Dong, D., Wang, C., Van Zwieten, L., Wang, H., Jiang, P., Zhou, M., & Wu, W. (2020). An effective biochar-based slow-release fertilizer for reducing nitrogen loss in paddy fields. *Journal of Soils and Sediments*, *20*(8), 3027-3040.
104. Salam, M. A., Mokhtar, M., Albukhari, S. M., Baamer, D. F., Palmisano, L., AlHammadi, A. A., &Abukhadra, M. R. (2021). Synthesis of zeolite/geopolymer composite for enhanced sequestration of phosphate (PO43−) and ammonium (NH4+) ions; equilibrium properties and realistic study. *Journal of Environmental Management*, *300*, 113723.
105. Palanivell, P., Ahmed, O. H., Omar, L., & Abdul Majid, N. M. (2021). Nitrogen, phosphorus, and potassium adsorption and desorption improvement and soil buffering capacity using clinoptilolite zeolite. *Agronomy*, *11*(2), 379.
106. Hagab, R. H., Kotp, Y. H., &Eissa, D. (2018). Using nanotechnology for enhancing phosphorus fertilizer use efficiency of peanut bean grown in sandy soils. *Journal of Advanced Pharmacy Education & Research| Jul-Sep*, *8*(3), 59-67.
107. PANDIT, V., JEEVAN, R., & NAIK, R. (2021). Effect of different levels of nitrogen and zeolite on nutrient uptake and nitrogen use efficiency in rice. *Journal of Crop and Weed*, *17*(2), 01-08.
108. Omar, L., Ahmed, O. H., &Majid, N. M. A. (2018). Amending chemical fertilizers with rice straw compost and clinoptilolite zeolite and their effects on nitrogen use efficiency and fresh cob yield of Zea mays L. *Communications in Soil Science and Plant Analysis*, *49*(14), 1795-1813.

109. Zheng, J., Chen, T., Chi, D., Xia, G., Wu, Q., Liu, G., ...&Siddique, K. H. (2019). Influence of zeolite and phosphorus applications on water use, P uptake and yield in rice under different irrigation managements. *Agronomy*, *9*(9), 537.
110. Uygur, V., Celik, C. S., Sukusu, E., &Mujdeci, M. (2017). The effect of particle size on phosphorus adsorption kinetic and desorption by turkish natural zeolites. *Fresenius Environmental Bulletin*, *26*(10), 6253-6260.
111. Hassan, A. Z. A., Mahmoud, A. W. M., &Turky, G. (2017). Rice husk derived nano zeolite (AM 2) as fertilizer, hydrophilic and novel organophillic material. *American Journal of Nanomaterials*, *5*(1), 11-23.
112. Ahmad, A., Ijaz, S. S., & He, Z. (2021). Effects of zeolitic urea on nitrogen leaching (NH4-N and NO3-N) and volatilization (NH3) in spodosols and alfisols. *Water*, *13*(14), 1921.
113. Hassan, A. Z. A., & Mahmoud, A. W. M. (2013). The combined effect of bentonite and natural zeolite on sandy soil properties and productivity of some crops. *Topclass Journal of Agricultural Research*, *1*(3), 22-28.
114. Kocar, G. (2012). The use of anaerobically digested slurry combined with natural zeolite for rapeseed production. *Energy Education Science and Technology Part A: Energy Science and Research*, *30*(1), 545-552.
115. Campisi, T., Abbondanzi, F., Faccini, B., Di Giuseppe, D., Malferrari, D., Coltorti, M., ...&Passaglia, E. (2016). Ammonium-charged zeolitite effects on crop growth and nutrient leaching: greenhouse experiments on maize (Zea mays). *Catena*, *140*, 66-76.
116. Lei, Z., Cagnetta, G., Li, X., Qu, J., Li, Z., Zhang, Q., & Huang, J. (2018). Enhanced adsorption of potassium nitrate with potassium cation on H3PO4 modified kaolinite and nitrate anion into Mg-Al layered double hydroxide. *Applied clay science*, *154*, 10-16.
117. Costamagna, G., Chiabrando, V., Fassone, E., Mania, I., Gorra, R., Ginepro, M., &Giacalone, G. (2020). Characterization and use of absorbent materials as slow-release fertilizers for growing strawberry: Preliminary results. *Sustainability*, *12*(17), 6854.
118. Yuvaraj, M., & Subramanian, K. S. (2018). Development of slow release Zn fertilizer using nano-zeolite as carrier. *Journal of plant nutrition*, *41*(3), 311-320.
119. Hoeung, P., Bindar, Y., &Senda, S. P. (2018). Development of granular urea- zeolite slow release fertilizer using inclined pan granulator. *JurnalTeknik Kimia Indonesia*, *10*(2), 95-101.
120. de Campos Bernardi, A. C., Oliviera, P. P. A., de Melo Monte, M. B., & Souza- Barros, F. (2013). Brazilian sedimentary zeolite use in agriculture. *Microporous and Mesoporous Materials*, *167*, 16-21.
121. Manikandan, A., & Subramanian, K. S. (2016). Evaluation of zeolite based nitrogen nano-fertilizers on maize growth, yield and quality on inceptisols and alfisols. *Int J Plant Soil Sci*, *9*(4), 1-9.
122. Yuan, J., Yang, J., Ma, H., & Chang, Q. (2017). Preparation of Zeolite F as Slow Release Fertilizers from K-Feldspar Powder. *ChemistrySelect*, *2*(33), 10722-10726.
123. Maharani, D. K., Dwiningsih, K., Savana, R. T., &Andika, P. M. V. (2018, December). Usage Of Zeolite And Chitosan Composites As Slow Release Fertilizer. In *International Conference on Science and Technology (ICST 2018)* (pp. 179-182). Atlantis Press.
124. Chawakitchareon, P., Anuwattana, R., &Buates, J. (2016). Production of slow release fertilizer from waste materials. In *Advanced Materials* (pp. 129-137). Springer, Cham.
125. Hoeung, P., Bindar, Y., &Senda, S. P. (2018). Development of granular urea- zeolite slow release fertilizer using inclined pan granulator. *JurnalTeknik Kimia In*
126. Zhou, H., Bhattarai, R., Li, Y., Li, S., & Fan, Y. (2019). Utilization of coal fly and bottom ash pellet for phosphorus adsorption: Sustainable management and evaluation. *Resources, Conservation and Recycling*, *149*, 372-380.*donesia*, *10*(2), 95-101.
127. Bhardwaj, D., Sharma, P., Sharma, M., &Tomar, R. (2014). Removal and slow release studies of phosphate on surfactant loaded hydrothermally synthesized silicate nanoparticles. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(5), 2649- 2658.