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REVIEW

An overview of zeolites synthesised from coal fly ash and their potential for extracting heavy metals from industrial wastewater

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ABSTRACT

Zeolites are aluminosilicate minerals widely used in industrial applications including as commercial adsorbents and catalysts. This overview focuses on zeolites synthesised from coal fly ash (CFA). Human activities and industrial developments generate large volumes of polluted water, which have a significant ecological impact. Industrial wastewater may consist of different pollutant types, but of specific interest to this work are heavy metals, which. Heavy metal ions are among the most dangerous pollutants due to their toxicity and carcinogenicity. This overview covers the recent scientific literature, focused on using CFA-derived zeolites to remove Ni, Hg, Mn, Cu, Zn, Cd, Pb, Cr, Co both from synthetic solutions replicating industrial wastewater and actual wastewater streams. The results described in many papers cited in this review look promising for industrial wastewater treatment operations. Furthermore, the large variety of possible synthetic zeolites provides a route for energy-efficient, pollutant-specific remediation of industrial heavy metals.

1. Introduction

1.1. History of zeolites

The knowledge of zeolites dates from 1756 when they were first mentioned by Swedish mineralogist Axel Fredrik Cronstedt [1]. Zeolite research progressed for centuries, and by the mid-1930s, researchers had published the ion exchange, adsorption, molecular sieve, and structural properties of zeolite minerals [2]. The next big step was when Cambridge University chemist Richard Barrer began his work with zeolite adsorption and synthesis in the mid-1930s to 1940s [2]. Barrer presented the first classification of zeolites in 1945 based on their molecular size [3] and the first definitive technique for the synthesis of zeolites in 1948 [4]. His pioneering work in adsorption and synthesis began the era of synthetic zeolites [2,5]. Currently, 255 natural and synthetic zeolite frameworks types are present in the database of zeolite structures by the International Zeolite Association (IZA) [6].

Zeolites possess good mechanical and thermal properties and high sorption capacity. Additionally, they may slightly adjust the pH of a soil or aqueous system [7]. Due to their catalytic properties, zeolites are widely used in the field of heterogeneous catalysis [8], as essential catalysts [9]. Zeolites are also used in many industrial processes and play a role in many large scale industrial applications [9]. Other zeolite applications are ion exchange, separation, adsorption, host/guest chemistry, microelectronic devices, optics, medicine, and membranes [10–12]. Though zeolites' primary use is in catalytic processes, zeolites are promising materials for sustainable development and energy conservation [8,11]. Additionally, natural and modified zeolites are low-cost due to their high availability in many parts of the world and are environmentally safe to use [7].

1.2. Zeolite types

Zeolites are made of a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral referred to as T atoms, linked at the corners by sharing oxygen atoms that form a three-dimensional network with numerous voids and open spaces [13]. These voids are the source of many

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unique zeolites properties, such as selectivity of molecules in adsorption process, catalytic properties and others [13].

Zeolite frameworks can be broken down into rings of different sizes, which correspond to the pore opening windows. Based on their maximum pore size, zeolites are categorised as small-pore (8-ring), medium-pore (10-ring), large-pore (12-ring), and extra-large-pore zeolites (>12-ring) [14]. The zeolite framework's negative charge is usually compensated by extra-framework mono-or di-valent cations, which can be exchanged for other cations [14]. The pore structure of zeolite depends on their type [15]. Examples of different zeolite structures and their respective pore sizes of commonly used zeolites are given in Figure 1 [14].

1.2.1. Natural zeolites

The regular formula of natural zeolites is $M_{x/n}[(AlO_2)_{x}\cdot(SiO_2)_y]\cdot wH_2O$ [16] where M is an alkali or alkaline-earth cation, n is the cation charge, w is the number of water molecules per unit cell, x and y comprise the total number of tetrahedra per unit cell; the ratio y/x usually has values ranging from 1 to ∞ [17,18].

Natural zeolites are porous, hydrated aluminosilicate minerals [19]. They form hydrothermally when hot water reacts with volcanic ash or lava [20]. These materials possess unique physicochemical properties, such as cation exchange capacity, large surface area, molecular sieving, catalysis, and sorption [21–24]. Currently, there are more than 45 natural zeolite types known [25], with the more common forms being chabazite, erionite, mordenite, and clinoptilolite [2,26].

Natural zeolites' unique physical and chemical properties make them useful in a wide range of applications including wastewater treatment [27], agriculture [28], fertilisers [29], aquaculture [28], animal health [30], animal nourishment [31], gas separation [32,33], solar refrigeration [33], gas cleaning [34], deodorisation [35], solid electrolytes [36], construction materials [37], and cleanup of radioactive wastes [27,38]. Natural zeolites used for environmental applications have received more attention from researchers due to their relative low cost [7,39], unique properties and broad worldwide occurrence [19]. In 2020 the worldwide mine production of zeolite was 1.1 million tons according to the USGS [40].

Although natural zeolites' features make them useful for a wide variety of purposes, their applications are limited by their microstructures and surface chemistry [16,41]. It is possible to control zeolite porosity, surface chemistry, and structure by various modification methods [41], including physical and chemical modification [16,41,42]. Natural and modified zeolites' sorption

capacity cannot compete with synthetic zeolites with designed composition, structure, and properties [39].

The focus of this overview is on synthetic rather than natural or modified zeolites. For a detailed description of natural zeolites' structures, physicochemical properties, and uses, readers are referred to Wang et al. [19]. For further information on modified zeolites, readers are referred to Kuhl et al. [16], Shi et al. [41] and Karge et al. [43].

1.2.2. Synthetic zeolite

The broad range of zeolite applications results from the various morphologies, pore sizes, and channel types [44,45]. As such, there is value in developing synthetic approaches to control crystal size and zeolite morphology [45,46]. In laboratory conditions, it is possible to emulate the natural process to form a zeolite [47]. Furthermore, zeolites can be synthesised with desired chemical properties and pore size [47]. There are multiple methods for zeolite synthesis [48], a selection of which will be covered in Section 2.

All synthesis reactions require appropriate equipment, clean substrates, and energy, all of which affect the economics and use of synthetic zeolite versus natural zeolite [47]. Despite that, the variety of zeolite-dependent processes is high, leading many scientists to search for a sustainable, less expensive, and cleaner synthetic zeolite [49]. One of the most popular uses for synthetic zeolites is heterogeneous catalysis in various traditional and emerging catalytic processes [50]. Similarly, synthetic zeolites are also used for manufacturing membranes to process radioactive solutions [51] and the promotion for direct gasoline synthesis from syngas [52].

Environmental aspects of production currently take centre stage, leading to a trend for using natural or waste raw materials for zeolite synthesis [47]. Research on zeolite synthesis from fly ash is rapidly gaining momentum due to the environmental benefits of redirecting this abundant waste material [13].

2. Zeolite synthesis

For zeolite synthesis a source of Si and Al is required [53]. The synthesis process often utilises the following methods: hydrothermal [54], solvothermal [55,56] or ionothermal [57,58]. For all of these processes, there are three necessary steps for zeolite formation [59]: supersaturation, nucleation, and crystal growth [43,60]. Hydrothermal synthesis is one of the most common approaches for zeolite synthesis [61]. For a review of developments in hydrothermal chemistry from 1845 to 1937, readers are referred to Rabenau et al. [62]. For a review of zeolite hydrothermal synthesis in the
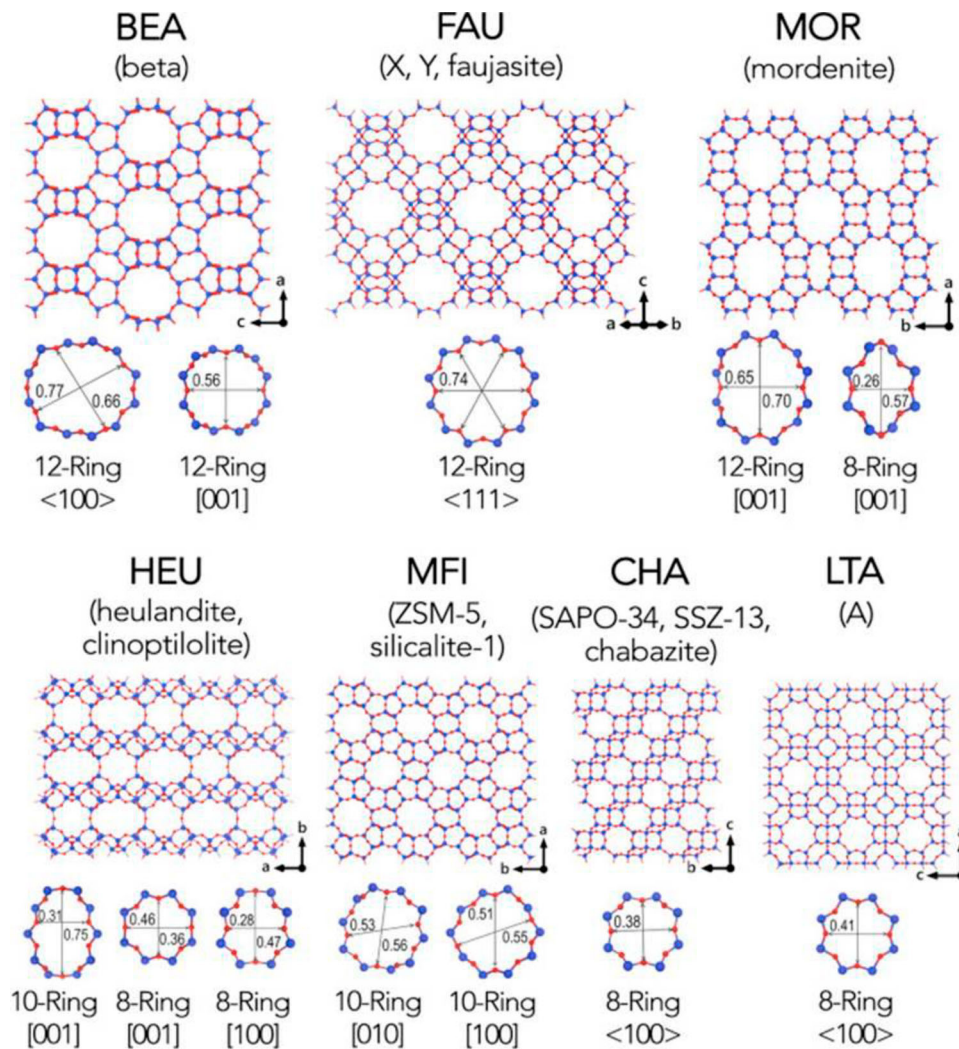
Figure 1. A selection of widely used Zeolite Framework Types, with their International Zeolite Association (IZA) three-letter code (in bold). Examples of zeolites in each category, pore size (in nm), and direction are given. The ball-stick models represent T atoms with blue spheres and red spheres represent oxygen atoms. Reproduced with permission from: Li et al. [14]. Data accessed November 2021.

second half of the twentieth century, see Cundy and Cox [54]. Of these methods, the hydrothermal method is the one most commonly used for zeolite synthesis [63]. It involves heating aqueous solutions of silica and alumina in an alkaline environment, commonly in sealed vessels to create autogenous pressure as the temperature rises. Structure-directing templates such as organic molecules and specific cations can also be included to control which form of zeolite is produced [59].

The zeolite crystal morphology produced using the hydrothermal method depends on [64–67]:

- the pH of the reaction mixture;
- process temperature and pressure;
- equilibration period and reaction time;
- reaction mixture composition, including structure-directing cations;
- any pretreatment applied.

Cundy and Cox [68] proposed a mechanism describing zeolite synthesis, which is currently the accepted model for these reactions. In brief, the model describes the equilibrium systems between an amorphous gel phase and the alkaline solution, which are conjugated to the ordered phase, the zeolite. The authors provide a detailed thermodynamic and kinetic treatment of the various reactions involved in zeolite synthesis, summarised as [68]:

- amorphous material reaches equilibrium with anions and cations in solution
- a small area of local order forms (nucleation)
- this area of local order grows, consuming anions and cations from solution
- the amorphous phase and solution maintain equilibrium, thus dissolving the amorphous phase [68].

Based on this model, the main parameters which control the synthesis process are temperature, alkalinity, Si/Al ratio, cation content, and time [61]. Additionally, the model gives a quantitative description of the effect of temperature on Al–Si dissolution and reaction rate. Finally, the model points at a strong relationship between solution alkalinity and nucleation rate. Ostwald's rule of successive transformations describes how the early forming and potentially meta-stable phases (such as zeolites A, X, or P) can be replaced by more stable structures (such as sodalite) as time progresses. This is especially important in more alkaline systems where the increased hydroxide concentration accelerates the dissolution of meta-stable zeolites [54,69]. For a detailed view on zeolite frameworks and their properties, readers are referred to International Zeolite Association (IZA) [6].

For a detailed treatment of zeolite synthesis procedures, including verified protocols for acquiring specific zeolite frameworks, see Byrappa and Yoshimura [70]. The remainder of this overview will focus on zeolites generated from coal fly ash.

2.1. Coal fly ash

Coal has been used as a fuel since at least ancient Greek and Roman times [13]. Coal was formed millions of years ago from deposited vegetable matter that over time has been transformed by geological processes to a carbon-rich coal [13,71]. Coal is currently the most widely distributed fossil fuel worldwide and is used by many countries to produce electricity [72,73]. The industrial combustion by-product of pulverised coal in coal-fired power stations is called Coal Fly Ash (CFA) [27], produced at 1200–1700°C from the various inorganic and organic constituents of the feed coal and generated today in large quantities [74,75]. Consequently, CFA is a mineral waste and recognised as an environmental pollutant and a waste product [75].

Of relevant note is the UN Climate Change Conference (UKCOP26) which was held November 2021. During UKCOP26 the reduction of global coal production by 2040 was proposed [76]. However, some of the world's biggest coal-dependent countries, including India, China and the USA, did not support this statement. As such, CFA is expected to be a relevant environmental pollutant for decades to come, adding to the already present billions of tons of stockpiled fly ash [77].

CFA comprises the following minerals: quartz, mullite, subordinately hematite and magnetite, carbon, and a prevalent phase of amorphous aluminosilicate [78,79]. Although these constituents are common to CFAs of all types, CFA chemistry is determined by the type of coal used [75]. Thus, more than 300 individual minerals and 188 mineral groups have been identified in different CFAs [80]. Approximately 750 million tonnes of CFA is generated globally per year [75], and this number continues to increase with the growth in power demand [81]. CFA finds use in various applications. The most significant is in cement and concrete manufacturing, due to the considerable SiO_2 and Al_2O_3 content and its pozzolanic properties [27,82]. For a review of CFA applications in the construction industry, including cement and concrete production, readers can refer to Kelechi et al. [83]. However, this application is limited to the demand for building materials [82]. For a detailed review of CFA used in the removal of both inorganic and organic pollutants, including heavy metals, dyes, pesticides, pharmaceuticals wastes and other pollutants readers are referred to a review paper by Singh et al. [84]. Additionally, Mushtaq et al. [85] looked at the potential applications of CFA as a photocatalyst, Fenton catalyst, membrane filter, and adsorbent in wastewater treatment.

CFA's use has significant economic and environmental implications and has become an increasing concern [86,87]. This massive amount of CFA industrial waste could cause significant environmental, ecological problems if not appropriately remediated [88] and may cause health issues [81], including chronic bronchitis, asthma, premature death, and lung cancer [61]. The forecast predicts power generation capacity to double in the next 30 years [89]. Even though many countries are moving away from using fossil fuels for energy, the historical volume of CFA and ash ponds are still an issue and can cause severe environmental problems, especially groundwater pollution [90].

With this production, a CFAs will need to be processed; unfortunately, CFA disposal methods are expensive [75,91,92], leading many researchers to look for a better way to utilise CFA waste [86,93]. For a detailed breakdown of CFA production and utilisation by country as of 2019, see Gollakota et al. [94] with the production and utilisation of fly ash by a selection of countries being given in Figure 2 [94].

The glass phase in CFA plays a vital role in zeolite formation because of its high solubility in an alkaline solution, making CFA well suited to zeolite synthesis [95–97]. Zeolite production has received a lot of interest [59,82] as they may be synthesised from CFA using a relatively cheap and fast conversion process [27]. These processes are covered in the following section.

2.2. Zeolite synthesis from CFA

Since the pioneering work by Holler and Wirsching [98], many researchers have synthesised different types of zeolites from fly ash [27]. Numerous methods have been proposed [99], varying the process by employing different alkaline solutions, alkaline agents' molarity, solution/solid ratio, temperature, time of reaction, pressure, and incubation type [74]. A few examples of zeolites synthesised from CFA include: Na–P1 [100], zeolite A [101,102], zeolite X [103,104] and zeolite ZSM-5 [105]. One major issue of zeolite synthesis from CFA is the large volume of potentially toxic coal-derived substances [102,106,107]. Toxicity in this instance is essentially of two forms. One form is due to the presence of heavy metals (Ni, Cd, Sb, As, Cr, Pb, etc.) generally found in fly ash. These metals do not degrade in biological systems and accumulate [108].

A number of methods are being proposed for extracting heavy metals from CFA. For example, Sahoo et al. [109] reviewed several hydrometallurgical methods developed for the recovery of metals from CFA. Similarly, Weibel et al. [110] investigated the extraction of heavy metals using hydrochloric acid and sodium chloride solution. Additionally, Leelarungroj et al. [111] looked into leaching mechanisms of As, Cr, Pb, and Zn from cement and fly ash stabilised soils. Readers are referred to Meer and Nazir [112] for a more thorough review of the methods used to remove heavy metals from fly ash, including leaching, biological processes, and other techniques.

Another form of toxicity is as a result of the fly ash's particle size (3–5 μm). Particles of this size can reach the pulmonary region of the human lungs and embed into them. Without a mechanism to clear these particles, they accumulate and act as cumulative poisons [113]. Furthermore, the submicron particles can penetrate deeper into the lungs and deposit on alveolar walls. Due to the high surface area in alveoli, metals can efficiently transfer to the blood plasma. Finally, the remaining particles (40–73% by mass), being mostly silica, may cause silicosis, a form of pulmonary fibrosis [113].

As previously mentioned in 2.1, CFA can be used as a feed stock in a range of applications, including construction industry and wastewater treatment. The functionality of CFA in these applications can be improved and diversified through beneficiation of CFA in to five streams: cenospheres, carbon concentrate, magnetic concentrate, fine products and coarse products [53]. Cenospheres are hollow ceramic spheres with a relative density <1 formed during the combustion process. These have applications as low-density fillers, and as a substrate for value added products. The carbon concentrate can be used as a high surface area substrates or adsorbents with lower cost and performance than activated carbon or reused as fuel. The magnetic fraction
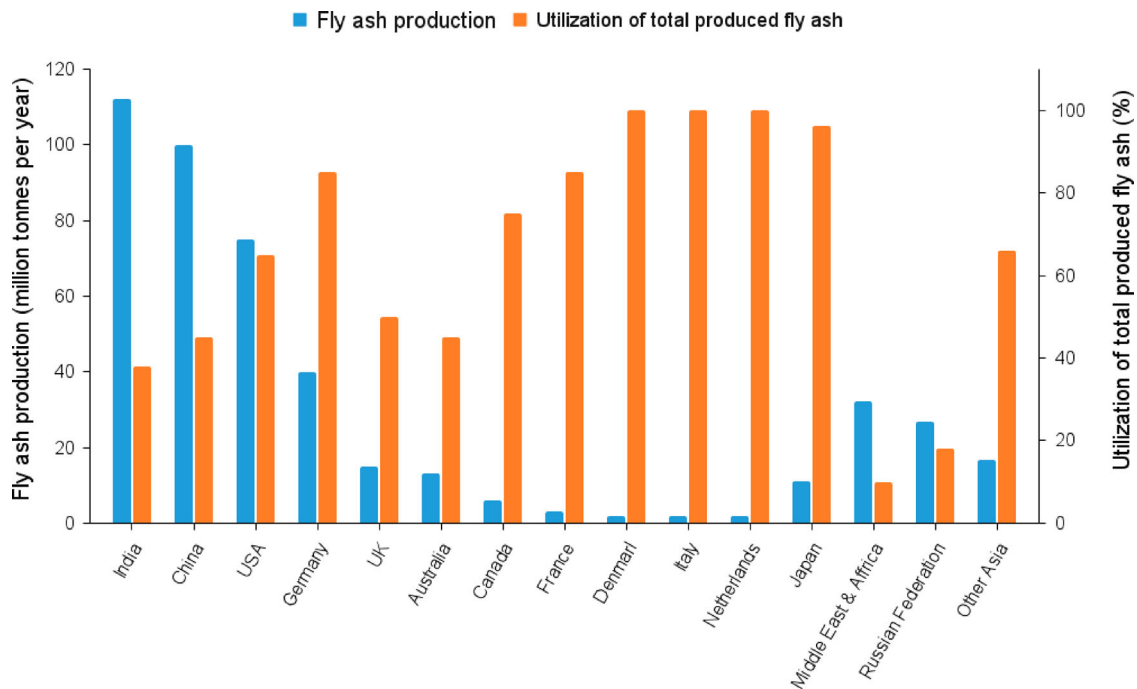

Figure 2. Fly ash production (million tonnes/year) and the utilisation of the produced fly ash for different countries, adapted from Gollakota et al. [94].

can be used where functional products with magnetic properties are desired, or as a filler, especially where high density or electromagnetic shielding properties are required. This fraction is also enriched in trace elements and comprises finer particles. The remaining material can be screened to produce a fine and coarse product. With the reduced LOI (below 5%) and fine particle size (<45 μm), the fine product surpasses ASTM C618-89 and BS EN450 requirements for use as a pozzolanic replacement for Portland cement in concrete, the removal of the magnetic concentrate improves also improves the whiteness of the concrete. The coarse material, rich in Al and Si, with a reduced concentration of other metals, can be used as an inert aggregate or filler and is a prime candidate for synthesis of zeolites [114]. Numerous researchers have examined the use of CFA for zeolite synthesis since it is rich in crystalline aluminosilicates [115]. This review is focused on the application of CFA-synthesised zeolites for heavy metal ion removal from water. The results of these studies will be covered in Section 3.4.

Zeolites can be synthesised under various conditions; however, the most widely used zeolite synthesis methods from fly ash are the hydrothermal and the fusion methods [74,116]. These two methods can be combined with microwave-assisted reactions to further control the reaction rate and zeolite morphology. Studies of zeolite synthesis with microwave-assisted heating showed significantly shorter synthesis times compared to conventional heating [82,117]. The control of experimental parameters and increased rate of formation afforded by microwave-assisted heating led to the development of various zeolites for extracting heavy metals from water. For example, Mishra and Tiwari [118] compared the adsorption of Cu^{2+}, Co^{2+}, and Ni^{2+} to fresh CFA. They found that the synthetic zeolite had a higher capacity than fly ash – the source material. Similarly, Hui et al. [102] investigated the performance and selectivity sequence of mixed heavy metal ions in an aqueous solution. This study compared zeolite A prepared from fly ash to commercial zeolite A, and residual products recycled from fly ash. They found that the Langmuir isotherm well described the equilibrium data and showed the affinity order: Cu^{2+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Ni^{2+}.

In conjunction with the development of synthetic methods for making zeolites, research has been carried out on the potential applications of zeolites synthesised from fly ash [27]. The Al (III)/Si (IV) ratio in zeolite structure accounts for the high cation exchange capacity (CEC) of some of these zeolites, including NaP1, 4A, X, KM, F, chabazite, herschellite, and faujasite [27]. The use of these materials as molecular sieves for gas purification was investigated by Querol et al. [119] and Srinivasan et al. [120].

In contrast with these hydrothermal methods, Park et al. [121] developed a technique of thermally treating CFA with a base and a salt. The cooled products were crushed and washed to remove unreacted bases and salts. The authors suggest the structure-directing nature of the chosen salts play a significant role in the zeolites formed, as indicated by the predominance of cancrinite produced by a NaOH-KNO₃ process, compared to sodalite in a NaOH-NaNO₃ process. The molten salt method is limited by high temperature requirements, long activation periods, and a low selectivity for high CEC zeolites [122]. The method has not been widely investigated by other authors. For further information, readers are referred to work on dry or molten-salt conversion by Berkgaut and Singer [100] and Park et al. [123].

The following sections detail recent studies that have utilised most popular synthesis methods for synthesising zeolites from CFA.

2.2.1. Hydrothermal method

In the late twentieth century, a variety of hydrothermal activation methods for synthesising different zeolites from coal fly ash were proposed [124–127].

Most of the proposed approaches control the dissolution of the Al–Si amorphous phase present in the CFA using hot alkaline solutions, mainly NaOH and KOH. In Figure 3 this described as the leaching process, and produces a supersaturated solution from which zeolites can be precipitated (crystallization process in the same figure), following hydrothermal synthesis routes described in Section 2.

Zeolite synthesis is highly sensitive to initial conditions, such as nucleation rate, source material and activation solution/source material ratio, and leads to significant variations in synthesis results. Blissett et al. [75] showed that up to 13 different zeolite types can be synthesised from the same CFA sample, by controlling these parameters. In general, they found that high activation temperatures (Figure 3 T2) and alkaline conditions (200°C and 5 M NaOH) led to low CEC zeolite formation. Conversely, lower temperature and alkalinity (<150°C and 0.5–3 M) led to the formation of high CEC zeolites [75].

This distinction between low and high-temperature synthesis leads to process economics issues, as the low CEC morphologies are prevalent when the rate is increased by heating. As such, an important issue for commercial zeolite production is how to speed up the production of desired species [75]. Therefore, a faster synthesis process is preferable, one that sidesteps the

expensive, high-temperature process, limiting the achievable morphologies [102,128]. However, Hui and Chao [129] successfully synthesised zeolite A by heating the crystallization solution to 90°C to encourage nucleation (T3 in Figure 3), which was followed by a temperature increase to 95°C (T4 in Figure 3) to promote crystal growth [61]. Other authors used microwave-assisted heating to promote crystal growth after a conventionally heated nucleation period [130]. This process produced zeolite A faster than a conventionally heated crystallization process [130]. Querol et al. [131] reported using microwave-assisted and conventional methods with similar yields and zeolite types, while the activation time required for microwave-assisted synthesis was significantly reduced: 30 min instead of the conventional 24–48 h. Kim and Lee [130] and Tanaka et al. [132] also used microwave-assisted heating, combining it with two-step silica extraction, and reported the production of high-quality zeolite A.

Hydrothermal methods easily dissolve the amorphous Si and Al content of CFA, but crystalline material such as quartz and mullite will not readily dissolve, and will remain as an impurity in the finished zeolite product [133].

Approach to improve zeolite purity is to filter out undissolved CFA between the dissolution and crystallization steps. Hollman et al. [134] proposed a two-stage hydrothermal method. The first step aims to obtain a Si-rich solution by dissolving Si from CFA by dissolution in NaOH. This is then filtered to remove undissolved fly ash, and stop zeolite formation. Thus in Figure 3 the leaching and crystallization steps take place separately. The second step is to adjust the Si:Al molar ratio through the addition of an Al source such as sodium aluminate [135–137]. Zeolite can then be crystalised under static conditions during hydrothermal treatment at <100°C [104,138,139].

For the leaching process, a variety of authors [129,134,140] used 2 M NaOH at 90–100°C, with solids loadings of 40–400 g CFA/L. Kim and Lee [130] investigated 1–5 M NaOH for leaching, followed by filtering, dilution, and adjustment of Si/Al ratio and NaOH concentration prior to crystallization. These experiments were compared to microwave-assisted leaching, which was found to increase the yield of Si and Al in the leachate, from 10 and 10% respectively through hydrothermal extraction to 35 and 20% using microwave-assisted extraction.

These leachates can then be used to crystallize zeolites through hydrothermal methods, with Hollman et al producing zeolite P, X, and A with sodalite through control of the Si/Al ratio (2:1, 1.8:1, and 1.2:1) and duration of crystallization (48, 48, and 67 h). Fukui et al altered the Si/Al ratio by adding rice husk ash (RHA) prior to the crystallization step. RHA is rich in Si, and this caused the Si/Al ratio to increase, resulting in the synthesis of phillipsite and sodalite, rather than zeolite A, X, and P which have a significantly higher Al content. Hui and Chao added an aluminium solution to their leachate before ageing it for 30 min at RTP. (Figure 3 T3). The solution was heated in two stages, firstly for 1.5 h to 80–90°C (Figure 3 T4) to allow nucleation to occur, and then to a higher tempterature of 90–95°C (Figure 3 T5) to encourage crystal growth and inhibit nucleation. This produced highly crystalline zeolites with a narrow particle distribution using a 30 min ageing step, a 90 min nucleation step at 90°C, and a 60 min crystal growth step at 95°C.

2.2.2. Alkaline fusion method

The fusion method was proposed by Shigemoto and Hayashi [141] to improve product purity. This approach's novelty was in introducing an alkaline fusion stage before the conventional zeolite synthesis [133]. In Figure 3 this is represented by the Fusion and dissolution steps which replace the leaching step. The main two differences of the fusion method compare to the classical hydrothermal method are:
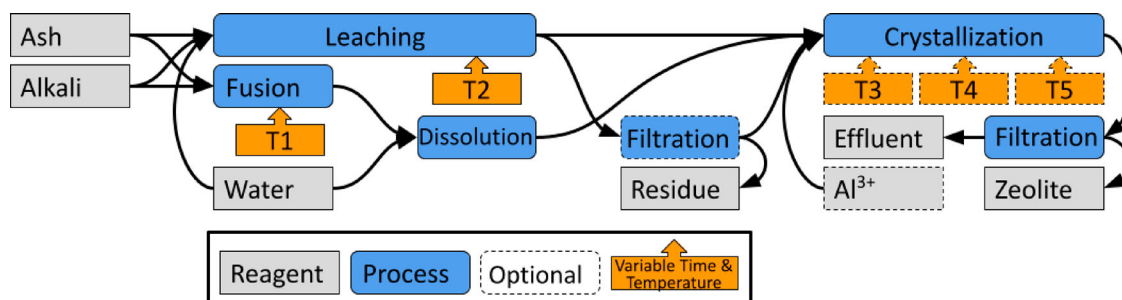

Figure 3. Unit operations in hydrothermal synthesis of zeolites from CFA.

- mixing and grinding CFA with a solid alkali in a ratio of 1:1.2 before heating to 500–550°C [133,141], for 1–2 h [100] (Figure 3 T1);
- grinding or crushing the cooled fusion product, and dissolving in water, distilled water, or seawater [74].

Molina and Poole [133] compared the CEC's of zeolites formed through conventional hydrothermal methods, and alkaline fusion methods at a variety of NaOH:CFA ratios. The authors concluded that the CEC of zeolites produced with an alkaline fusion step were higher than those produced through the hydrothermal method alone. The authors also concluded that the optimum NaOH:CFA ratio was 1.2:1, with lower ratios producing less crystalline zeolite X, and higher ratios producing a mixture of zeolite X and sodalite, or sodalite alone.

After the fusion process, the CFA has been converted to water-soluble species such as sodium aluminosilicate and sodium silicate [100,142–145]. This fusion product is broken up and then dissolved. Commonly this dissolution occurs at room temperature and pressure overnight, or for 12–24 h [100,133,142,145]. In lieu of distilled water, seawater can be used to reduce material and energy costs, reduce consumption of potentially potable water, and to benefit from the presence of NaCl which can aid the crystallisation process [68,146]. Berkgaut and Singer [100] studied the effect of an ageing step, where the solution is kept at room temperature for 12 h prior to hydrothermal crystallization at 100°C. The unaged sample produced zeolite P whilst the aged sample produced zeolite X.

After the dissolution process, zeolite crystallization can be performed using methods similar to the hydrothermal methods described earlier. Work by Belviso et al. showed that the use of seawater as a dissolution medium lowered subsequent temperatures required to crystallize zeolites, and Ca and Mg were sequestered during the crystallization process of zeolite X. This supports the idea that cations perform a structure-directing role during zeolite synthesis.

Izidoro et al. [147] were able to achieve complete conversion of CFA into zeolite A or X by variation of crystallization conditions. Complete conversion was confirmed by the lack of mullite or quartz in XRD analysis, and lack of other materials in SEM images. During the dissolution process, the authors altered the solid/liquid ratio, and during the crystallization process, the authors altered the Si:Al ratio with additional sodium aluminate, and varied the duration of the crystallization process to produce either zeolite X or zeolite A. Zeolite X was produced with a lower solids loading, less additional Al, and longer crystallization time compared to conditions required to produce zeolite A.

In conclusion, the most significant variables in the alkaline fusion method are:

- NaOH:CFA ratio has an optimum value of 1.2:1; other ratios will produce zeolties but the CEC may be lowered.
- Solids loading during the 'dissolution' step will affect the pH of the solution, and concentration of Si and Al.
- Choice of solvent. Using seawater provides NaCl to assist crystallization, and other structure-directing cations.
- Si/Al ratios, temperatures and durations applied during the crystallization phases are relevant here as they are to the hydrothermal method.

Ayele et al. [148], Shigetamo et al. [141], and Kumar et al. [149] investigated the topic of synthesis by fusion. Further improvements on the base method have been proposed by Ozdemir et al. [81], who follow the **A**lkaline **F**usion with the **U**ltrasonic-assisted synthesis **M**ethod (AFUM). This shortened the time required to synthesise zeolite X.

3. Zeolite applications in water treatment

3.1. Water pollution

Water is an irreplaceable and essential resource [150,151]. Human activities and industrial developments generate large volumes of polluted wastewater, which is a severe environmental problem [152,153]. Water pollution is one of the leading reasons for water shortages [154] and can also affect other significant aspects of our life, such as public health, industrial and agricultural production, and the economy [155].

There are a wide range of factors generating water pollution worldwide [156]. Industrial wastewater may consist of different pollutant types depending on the generating process [150]. The most common pollutants in wastewaters are specific organic constituents, high salinity, and heavy metals [150]. A more detailed review of water pollution types (i.e. chemical pollution, toxic pollutants, groundwater, etc.) and available wastewater treatment technologies, can be found in [156–158]. The remainder of this overview focuses on the use of zeolites synthesised from CFA to remove heavy metal ions from aqueous solutions.

The term heavy metals is often used as a group name for metals and metalloids that have been associated with contamination and potential toxicity in the

environment [159,160]. Heavy metals can be divided into three groups, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru, etc.) and radionuclides (such as U, Th, Ra, Am) [161]. They are considered as one of the most dangerous groups of pollutants [162] because they are not biodegradable and tend to accumulate in living organisms [163]. Furthermore, conventional wastewater treatment methods might be challenging to apply to heavy metals removal due to their high stability and solubility [163]. Heavy metals pollute the environment through wastewater originating through many sources including metal plating facilities, mining operations, agriculture, fertiliser production, tanneries, batteries, paper industries and pesticides, battery manufacturing, textile printing, and leather industries [162,164].

3.2. Heavy metal ions remediation

There are various methods available to reduce heavy metal concentrations in wastewater, including: chemical precipitation [165–167], ion exchange [168,169], photocatalysis [170], electrocoagulation [171,172], electrochemical treatment [173], adsorption [174], membrane filtration [175], reverse osmosis [176,177], bioadsorbents [161,178], coagulation and flocculation [179], flotation [106,164], solvent extraction [107] among others [150,164].

Adsorption is often considered the most effective method due to its high efficiency for removing low but still toxic concentrations heavy metals [102,162,164]. Adsorption provides flexibility in design, high-quality treated effluent; it is reversible, and the adsorbent can be regenerated [164,180,181].

3.3. Zeolite applications in water treatment

Zeolites are often considered a low-cost adsorbent for heavy metal remediation due to limitations and high cost of other popular adsorbents such as activated carbon, alumina, and silica [164,182]. Zeolites have unique ion exchange and adsorption properties, high porosity and thermal stability and as such are highly suitable for water treatment processes [183–185].

Furthermore, their net negative charge is balanced by the exchangeable cation, which has been demonstrated with Pb, Cd, Zn, Fe, Cu, and Mn ions [186,187]. These ions are of specific interest due to their detrimental environmental and health impacts [186].

For a review of natural and modified zeolites remediation of various chemical pollutants from water and wastewater, see Wang and Peng [19]. For a review of surfactant modified zeolites used for the removal of heavy metals from water, please refer to Jimenez-Castaneda et al. [188], Howard et al. [189], Erdem et al. [190], and Blanchard et al. [191].

3.4. CFA synthesised zeolites for heavy metal ion remediation

As this overview is aiming at focusing specific heavy metals and their mixtures, the remainder of this paper will contrast studies on single cation remediation and compare them to mixed-species studies. Publications from the 1990s to 2022 are described, all of which investigated metal ion adsorption onto zeolites synthesised from coal fly ash. The results of these studies are presented in this section and summarised in Tables 1–9 for single-ion systems and Table 10 for mixed-ion systems.

3.4.1. Nickel

When considering Ni remediation from single cation solutions, He et al. [154] showed that A-type CFA synthesised zeolite can achieve efficiencies of up to 94% removal of Ni^{2+} ions from solution with calculated adsorption capacity of 47 mg/g from 100 mg/L Ni^{2+}. Similarly, Zhang et al. [192] demonstrated that zeolite X can achieve up to 95% nickel removal with a capacity of 16 mg/g.

Sireesha et al. [193] modified CFA with zeolite (FA-Z) and investigated its efficiency in Ni and Cd ions removal from aqueous solutions in both single and mixed-ion system. Thus for Ni^{2+} the maximum adsorption capacity was found 61 mg/g and for Cu^{2+} 96 mg/g or 99% and 97%, respectively. The efficiency of FA-Z with in removing Ni^{2+} and Cu^{2+} in mixed ion solution and in real effluent was found at ~60% and ~95%, respectively. Furthrmore, Sireesha et al. [193] investigated both batch and column systems, and column system was identified as a more sufficient method. They also investigated the desorption of metal ions from zeolite surface using H_2SO_4.

Other studies focused on mixtures of heavy metal ions, including Ni. These studies have shown that Ni adsorption efficiency is low in the presence of other metal ions. As such, Visa et al. [194] investigated the efficiency of novel zeolitic materials (ZCET40 and ZDs40) synthesised from fly ash for the removal of Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} from single and mixed-ions synthetic solutions. It was shown that Ni is poorly adsorbed by both type of zeolites as long as other ions remain in solution due to the competitive mechanisms of heavy metals for the similar adsorption sites on the zeolite.

Similarly, Hui et al. [102] synthesised pure and chamfered-edge type 4A zeolites prepared from CFA, and studied them for the adsorption of mixed metal ions (Co^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}) solutions. The highest equilibrium sorption was obtained for Cu at 50 mg/g, which decreased to 42 mg/g for Cr^{3+}, 31 mg/g for Zn^{2+}, 14 mg/g for Co^{2+}, and 9 mg/g for Ni^{2+}. Similarly, for commercial zeolite 4A, the greatest equilibrium sorption capacity obtained was, in mg/g, 53 (Cu^{2+}), 45 (Cr^{3+}), 32 (Zn^{2+}), 12 (Co^{2+}), and 8 (Ni^{2+}).

Additionally, He et al. [195] studied the maximum adsorption capacities of CFA zeolite prepared using the fusion method. This study worked with single and mixed cations in aqueous solutions focusing on Pb, Cu, Cd, Ni, and Mn ions. It reported, that the absolute Ni^{2+} adsorption capacity is 34 mg/g for a single ion system and 16 mg/g in a multi-ion system with an adsorption efficiency of $85 \pm 0.5\%$ in a multi-ion system. In this work, it was indicated that the main factor impacting the selectivity adsorption was the hydrolysis constant.

Alvarez-Ayuso et al. [196] investigated the sorption behaviour of natural (clinoptilolite) and synthetic (NaP1) zeolites for Cr^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} from wastewater. Maximum adsorption capacities achieved were, in mg/g, 44 (Cr), 20 (Ni), 33 (Zn), 51 (Cu), 51 (Cd) and 4 (Cr), 2 (Ni), 3 (Zn), 6 (Cu), 5 (Cd) for synthetic and natural zeolites, respectively. The sorption capacities shown by the synthetic zeolites were approximately 10 times greater than those shown by natural zeolite also investigated in this study. This could be explained by a higher H^+ exchange capacity and higher cation exchange capacity of synthesised zeolites.

In summary, Ni ions are adsorbed well by multiple zeolite types, although they have reduced removal efficiencies in multi-ion solutions. Some of this effect could be attributed to competition with other species in solution. Furthermore, a significant effect on removal efficiency could be observed due to pH. Consequently, controlling for pH during remediation of multi-ion systems is a significant factor in achieving a given removal efficiency.

For ease of comparison, the details of this section are condensed into Table 1 for single-ion solutions and Table 10 for mixed-ion solutions.

3.4.2. Copper

Wang et al. [116] compared zeolite A and zeolite X synthesised from CFA for Cu^{2+} ion removal from a Cu-Zn multi-ion system. In this study, zeolite A showed a maximum adsorption capacity of 38 mg/g for Cu^{2+} and 30 mg/g for Zn^{2+}. For zeolite X, the amount of Cu^{2+} adsorbed was 29, and 22 mg/g for Zn^{2+}.

He et al. [195] established a maximum adsorption capacity for Cu at 56 mg/g from a single-ion solution and 33 mg/g from a Pb, Mn, Ni, Cu, Cd system with an efficiency of $95 \pm 0.7\%$. Additionally, Hui et al. [102] showed that pure and chamfered-edge zeolite 4A prepared from CFA had adsorbed 50 mg/g of Cu^{2+} a multi-species solution containing of Co^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}.

Wang et al. [197] also used CFA derived zeolite for the removal of Cu^{2+}, Pb^{2+} and Cd^{2+} from water. The maximum adsorption capacity shown in this study was 10 mg/g for Cu^{2+}, 1 mg/g for Pb^{2+} and 0.3 mg/g for Cd^{2+}. Thus, the order of selectivity for metal ions showed in this study is $Cu^{2+} > Pb^{2+} > Cd^{2+}$.

Wu et al. [198] investigated Cu^{2+} and Cd^{2+} adsorption by zeolite synthesised from hydrothermally treated CFA. For each experiments, set of 50–500 mg/L metal concentration were prepared and 1 g/L of adsorbent was added. The pH was monitored to 6.0 ± 0.2 for all solutions. The sorption capacity of the synthesised zeolite at equilibrium was calculated to be 71 and 83 mg/g for Cu^{2+} and Cd^{2+}, respectively.

Yang et al. [199] compared CFA synthesised zeolite A with CFA synthesised zeolite modified with Fe_3O_4 (MFZ) for Cu removal from water. The adsorption capacity of synthesised zeolites was found as around 50 mg/g. Similarly, Wang et al. [200] used magnetic zeolite P synthesised from low-grade fly ash for the removal of Cu^{2+} and Pb^{2+} ions from a multi-ion aqueous solution. The saturation adsorption capacity of Cu^{2+} ions by magnetic zeolite P (synthesised from low-grade fly ash with iron oxide) and synthesised non-magnetic zeolite P were 25 and 30 mg/g, respectively. For Pb^{2+} adsorption by the non-magnetic zeolite was higher than the magnetic (28 and 20 mg/g, respectively). Even though the adsorption capacity of magnetic zeolite was lower than of non-magnetic, the induction of magnetic particles may make recovery of the used zeolite from wastewater easier by leveraging its magnetic properties.

Song et al. [201] investigated the ability of zeolite synthesised from CFA to adsorb Cu^{2+} ions. XRD results showed that the synthesised material has basic structural unit of microporous zeolite molecular sieves, and consist of zeolite 4A and zeolite X The maximum adsorption capacity at pH 5 and sorbent dosage of 4 g/L ranged from 69 mg/g at 20°C to 141 mg/g at 50°C.

For ease of comparison, the details of this section are condensed into Table 2 for single-ion solutions and Table 10 for mixed-ion solutions.

Table 1. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Ni.

Ion	Zeolite type	Surface area of zeolite, m²/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Ni	Zeolite A	90.04	NA	47	2	7	100	100	He et al. [154]
Ni	Zeolite X	NA	2.70	16	2.5	5	100	100	Zhang et al. [192]
Ni	CFA Zeolite	346.6	NA	61	5	5	10–500	100	Sireesha et al. [193]
Ni	CFA Zeolite	12.7	1.64	34	1	5	100	100	He et al. [195]
Ni	NaP1 Zeolite	27.7	1.95	20	2.5	6	100	20	Alvarez-Ayuso et al. [196]

3.4.3. Zinc

A novel method for metal ion adsorption from sewage using NaP zeolite synthesised from stage-treated CFA was proposed by Zhang et al. [202]. The study investigated the synthesis of NaP, NaP-AMP (2-amino-methyl-propyl alcohol), NaP-PEG (polyethylene glycol), NaP-CyOH (cyclohexanol) zeolites and their use in Zn^{2+} adsorption. NaP, NaP-AMP, NaP-PEG zeolites showed the adsorption capacity and removal of 37 mg/g (91.4%), 39 mg/g (96.8%) 35 mg/g (88%), respectively. NaP-CyOH zeolite showed the highest adsorption capacity of 40 mg/g and the removal of 99.9% due to it having the largest surface area of 80 m²/g vs 27 m²/g (NaP zeolite), 29 m²/g (NaP-AMP zeolite) and 24 m²/g (NaP-PEG zeolite).

Izidoro et al. [147] investigated zeolites X (ZXJL) and A (ZAJL) synthesised from CFA for Cd^{2+} and Zn^{2+} remediation. The study used several CFA source materials for synthesising the zeolites and measured their capacity and efficiency both from single and multi-ion systems. The maximum adsorption capacity for Zn^{2+} ions in a single ion solution varied from 156 (ZXJL) to 185 mg/g (ZAJL) and for Cd^{2+} from 205 (ZXJL) to 220 mg/g (ZAJL). For a two ion system, the adsorption capacities for zeolite X ranged from 58 to 70 mg/g for Zn^{2+} and from 60 to 72 mg/g for Cd^{2+}. For zeolite A, the values ranged from 89 to 90 mg/g for Zn^{2+} and from 174 to 195 mg/g for Cd^{2+} ions. Comparing the adsorption results of Cd^{2+} and Zn^{2+} ions between one and two ion solutions indicated that Cd and Zn adsorption percentages were strongly affected by the presence of competitor ions on zeolite X, while zeolite A still reached high adsorption percentages in the presence of the competing ions. In general, Cd^{2+} removal was more affected by the presence of Zn due to the preference for Zn^{2+} ions by the pure zeolites [147].

For ease of comparison, the details of this section are condensed into Table 3 for single-ion solutions and Table 10 for mixed-ion solutions.

3.4.4. Lead

He et al. [195] used CFA derived zeolite prepared using the fusion method, achieving capacities of 66 mg/g for Pb in single cation solutions and 45 mg/g in multiple-species solutions of Pb, Cu, Cd, Ni, and Mn ions with an efficiency of 93%.

Jangkorn et al. [203] synthesised Zeolite A from CFA (ZCF) and bagasse fly ash (ZBG) using alkaline fusion method was followed by hydrothermal synthesis. Additionally, they investigated adsorption capacity of ZCF and ZBG for Pb ions removal and both showed 100% efficiency. Thus, the maximum adsorption

Table 2. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Cu.

Ion	Zeolite type	Surface area of zeolite, m²/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Cu	CFA Zeolite	12.7	1.64	56	1	5	100	100	He et al. [195]
Cu	NaP1 Zeolite	27.7	1.95	51	2.5	5	100	20	Alvarez-Ayuso et al. [196]
Cu	CFA Zeolite	NA	NA	71	1	6	500	50	Wu et al. [198]
Cu	Zeolite A	NA	NA	50	NA	3	250	50	Yang et al. [199]
	Magnetic CFA – zeolites	NA	NA	49		3			
Cu	CFA zeolite	NA	NA	69–141	4	5	40–500	NA	Song et al. [201]
Cu	CFA Zeolite	346.6	NA	96	5	5	10–500	100	Sireesha et al. [193]

Table 3. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Zn.

Ion	Zeolite type	Surface area of zeolite, m²/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Zn	NaP1 Zeolite	27.7	1.95	33	2.5	6	100	20	Alvarez-Ayuso et al. [196]
Zn	NaP Zeolite	26.8	NA	37	2.5	5	100	20	Zhang et al. [202]
	NaP-CyOH	80.4		40					
	NaP-AMP	28.6		39					
	NaP-PEG	24.3		35					
Zn	Zeolite X	249.7	3.10	205	10	6.8	NA	50	Izidoro et al. [147]
	Zeolite A	15.7	3.90	220					

capacity of ZCF was found 556 mg/g at pH 5 while Pb ions concentration was 200 mg/L.

Kobayashi et al. [204] used a novel K-type zeolite synthesised from CFA for Pb^{2+} adsorption from aqueous solutions. The maximum adsorption capacity of the zeolite they synthesised was 20 mg/g meaning that 76% of Pb ions were removed from the solution with initial concentration of 50 mg/L. At the same time, the effect of coexisting ions on the adsorption capability of Pb^{2+} was investigated for Mg^{2+}, K^+, Ca^{2+}, Ni^+, Cu^{2+}, Zn^{2+}, Sr^{2+}, and Cd^{2+} as the components of the two cation solution. The adsorption capacity of other cations excluding Pb^{2+} was significantly lower than that of Pb^{2+}, meaning that the synthesised K-type FA48 zeolite exhibited selectivity for Pb^{2+} adsorption from a binary solution system containing other cations. This was explained by several factors, such as charge density and hydrated ion diameter, and the accessibility of the active sites of natural FA48 [205]. The hydrated ion radius and electronegativity of Pb^{2+} exceed those of cations such as Ni^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} [205,206].

Zeolites synthesised from low-calcium LCZ and high-calcium HCZ fly ash were investigated for the removal of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution by Ji et al. [207]. The maximum adsorption capacities in mg/g obtained for the removal of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}, were 156 (Zn^{2+}), 198 (Cu), 124 (Cd), and 186 (Pb) mg/g for LCZ and 154 (Zn), 183

(Cu), 119 (Cd), and 192 (Pb) for HCZ, respectively. This study showed that both low and high calcium coal fly ash have potential as effective adsorbents for the simultaneous removal of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} from an aqueous solution. However, if selectivity is required, these zeolites are not applicable.

Qiu et al. [208] synthesised zeolites from fly ash for multi-ion heavy metal solutions of Cd, Cu, Mn, Ni, Pb and Zn adsorption using municipal solid waste incineration fly ash by microwave-assisted hydrothermal treatment. The results showed that the adsorption capacity followed the order of Pb > Cu > Zn > Mn ≈ Ni > Cd. It was shown that with an increase in zeolite content, the adsorption of all metal ions improved as well. The highest adsorption capacity shown in this study, in mg/g, was 50 (Pb), 28 (Cu), 20 (Zn), 15 (Mn), 14 (Ni), 11 (Cd).

The adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+}, and Mn^{2+} using zeolites synthesised from Brazilian fly ash was studied by Nascimento et al. [209]. Their results showed that the maximum adsorption capacity of synthesised zeolite was, in mg/g, 195 (Pb), 77 (Cu), 60 (Mn), 59 (Zn). The adsorption increased up to 25 times compared to the original ash. The preferred order observed for adsorption was Pb > Cu > Mn ≥ Zn, meaning that synthesised zeolite is selective for Pb. Based on this study, part of the sorption properties of these ions are due to ion exchange with the zeolite. Specifically, Pb appears to

preferentially replace exchangeable cations (mainly sodium and calcium) in zeolite compared to Cu, Mn and Zn. Zeolites preference for Pb ions might be due to its lower dehydration energy and smaller hydrated radius [195].

Joseph et al. [210] investigated simultaneous removal of Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions from aqueous solutions via adsorption on FAU-type zeolites synthesised from CFA. The results showed that in the presence of competing ions, FAU zeolite sample CFZ10-68 simultaneously remove heavy metals from aqueous solution in the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+}$. The maximum adsorption capacity was found for Pb^{2+} 110 mg/g and for Co^{2+} 12 mg/g.

Similarly, Bai et al. [211] synthesised X-type zeolite from combination of CFA oil shale ash (OSA) using the alkaline fusion hydrothermal method and investigated its' use in water treatment from Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}. The study shows that the removal efficiency of the heavy metals increases with the increase of the amount of added adsorbent. Furthermore, the selectivity sequence was in following order: $Pb^{2+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$ with the maximum adsorption capacity of 112 mg/g (Pb^{2+}), 62 mg/g (Cr^{3+}), 54 mg/g (Cu^{2+}), 45 mg/g (Zn^{2+}) and 38 mg/g (Cd^{2+}). This result agrees with the order of the hydrated radius of the metals.

Lastly, Li et al. [212] used one-step hydrothermal method for synthesis of zeolites-calcium silicate hydrate composite from CFA with co-activation of $Ca(OH)_2$-NaOH. They investigated the materials adsorption capacities for single ion solutions of Pb^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Cr^{3+}. The maximum adsorption capacities were respectively found to be 409 mg/g (Pb^{2+}), 222 mg/g (Ni^{2+}), 148 mg/g (Cd^{2+}), 93 mg/g (Zn^{2+}), 101 mg/g (Cu^{2+}) and 157 mg/g (Cr^{3+}) at the pH of 4.5. At the same time, for mixed-ion system, the adsorption capacities were 122 mg/g (Pb^{2+}), 71 mg/g (Cr^{3+}), 34 mg/g (Cu^{2+}), 28 mg/g (Zn^{2+}), 10 mg/g (Cd^{2+}) and 5 mg/g (Ni^{2+}). Such difference can be explained by the competitive adsorption of these heavy metal ions in the order $Pb^{2+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$.

For ease of comparison, the details of this section are condensed into Table 4 for single-ion solutions and Table 10 for mixed-ion solutions.

3.4.5. Cadmium

Li et al. [213] presented a novel microwave assisted digestion, and alkali fusion assisted hydrothermal method for synthesising zeolite from CFA for Cd^{2+} ions remediation. The synthesised zeolite was identified as faujasite and showed an efficiency of 99% and a maximum adsorption capacity of 87 mg/g.

Remenarova et al. [214] used zeolitic materials ZM1 and ZM3 (synthesised by hydrothermal alternation from CFA with 1 and 3 M NaOH, respectively) for Cd^{2+} ion removal from aqueous solutions. The maximum adsorption capacities were calculated from Langmuir isotherms to be ∼696 μmol/g (78 mg/g) for ZM1 and ∼1160 μmol/g (130 mg/g) for ZM3.

For ease of comparison, the details of this section are condensed into Table 5 for single-ion solutions and Table 10 for mixed-ion solutions.

3.4.6. Other metals (Cr, Hg, Co, Mn)

3.4.6.1. Chromium. In addition to Cr adsorption investigated by Alvarez-Ayuso et al. [196] mentioned in Section 3.4.1, Wu et al. [215] investigated the ability of 14 zeolites synthesised from different fly ashes to remove Cr^{3+} from an aqueous solution. The maximum adsorption capacity of 51 mg/g was obtained at pH 4 ± 0.1 for high calcium Wujin F zeolite. Compared with the NaP1 zeolite, the small pore size of the hydroxysodalite of the Wujin F zeolite would promote selective sorption of chromium by hindering the sorption of relatively large ionic radius elements (Ca^{2+}, Mg^{2+}, Na^+, K^+, with Ca^{2+} and Na^+ the most abundant ions in solution).

Ghasemi et al. [216] used CFA synthesised NA-P1 type zeolites modified with Ammonyx KP (KP) and Hexamethylenediamine (HDTMA) modified zeolites for the removal of Cr^{6+} from aqueous solutions. The maximum adsorption capacities of zeolites synthesised in this study were 49 and 338 mg/g for KP-Na-P1 and HDTMA-Na-P1, respectively.

For ease of comparison, the details of this section are condensed into Table 6 for single-ion solutions and Table 10 for mixed-ion solutions.

3.4.6.2. Mercury. Attari et al. [217] compared the removal efficiency of Linde Type A zeolite synthesised from CFA and a commercial-grade activated carbon for mercury adsorption. Both adsorbents showed a similar equilibrium value close to 95% under the same experimental conditions with the maximum adsorption capacity of the zeolite being 0.4 mg/g.

A modified approach was attempted by Tauanov et al. [218] using coal fly ash-derived zeolites doped with silver nanoparticles. Their research showed that this nano-composite approach could remove 99% of Hg^{2+} in 1 day while fly ash derived zeolite without doping achieved only 91.3% efficiency after 14 days. The adsorption capacity of the zeolite and Ag-nanocomposite in 10 mg/L Hg^{2+} solution at pH 2.0 was measured to be 0.4 and 6 mg/g, respectively. Overall, while CFA derived zeolites are effective Hg adsorbents, composite approaches are showing higher efficiencies. That was

Table 4. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Pb.

Ion	Zeolite type	Surface area of zeolite, m^2/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Pb	CFA Zeolite	12.7	1.64	66	1	5	100	100	He et al. [195]
Pb	Zeolite A	10.4	NA	556	0.1	5	200	200	Jangkorn et al. [203]
Pb	K-type Zeolite (FA48)	47.3	0.986–0.999	56	0.2	2–5	50	50	Kobayashi et al. [204]
Pb	CFA Composite Zeolite	96.5	NA	409	0.5	4.5	100 ± 10	100	Li et al. [212]

Table 5. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Cd.

Ion	Zeolite type	Surface area of zeolite, m^2/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Cd	Zeolite X	249.7	3.10	156	10	6.6	NA	50	Izidoro et al. [147]
	Zeolite A	15.7	3.90	185					
Cd	CFA Zeolite	12.7	1.64	52	1	5	100	100	He et al. [195]
Cd	CFA synthesised Faujasite	75.7	NA	87	0.5	6	20	50	Li et al. [213]
Cd	NaP1 Zeolite	27.7	1.95	51	2.5	6	100	20	Alvarez-Ayuso et al. [196]
Cd	CFA Zeolite	NA	NA	83	1	6	500	50	Wu et al. [198]
Cd	Zeolitic material ZM1	NA	NA	71	2.5	6	450	300	Remenarova et al. [214]
	Zeolitic material ZM3	NA	NA	130					

Table 6. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Cr.

Ion	Zeolite type	Surface area of zeolite, m^2/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Cr	NaP1 Zeolite	27.7	1.95	44	2.5	4	100	20	Alvarez-Ayuso et al. [196]
Cr	High calcium Wujin F Zeolite	NA	< 3	51	10	4	400	40	Wu et al. [215]
Cr	KP-Na-P1	41.5	NA	49	0.5	2	50	100	Ghasemi et al. [216]
Cr	HDTMA-Na-P1		NA	338					

explained as a difference in adsorption mechanisms in Tauanov et al. [218]. The dominating mechanism of mercury uptake in zeolite is physical adsorption, whereas in the investigated Ag nanocomposites it is a combination of adsorption, redox reaction producing Hg°, and amalgamation [218].

Kobayashi et al. [219] synthesised K-type zeolite using CFA by hydrothermal treatment of CFA at different intervals. Representative sample FA48 was synthesised for a longest time compared to other zeolites in this study (48 h). It showed the highest adsorption efficiency for Hg^{2+} ions, indicating that the hydrothermal treatment time is important to enhance the adsorption capability of K-type zeolite. Additionally, desorption process was investigated showing that about 70% of Hg^{2+} ions could be desorbed using a sodium hydroxide solution.

For ease of comparison, the details of this section are condensed into Table 7 for single-ion solutions and Table 10 for mixed-ion solutions.

3.4.6.3. Cobalt. Lee et al. [220] studied the adsorption of cobalt ions on zeolite synthesised from CFA. The results showed that maximum adsorption capacity for Z-C1 synthesised zeolites was 94 mg/g.

As was mentioned in Section 3.4.1, Hui et al. [102] investigated adsorption capacities of zeolite A prepared from fly ash in solutions with the presence of Cu^{2+}, Cr^{3+}, Zn^{2+}, Co^{2+}, Ni^{2+} ions. The maximum adsorption capacity for Co^{2+} was found as 14 mg/g and the selectivity sequence was in the following order $Cu^{2+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Ni^{2+}$. Similarly, Joseph et al. [210] investigated simultaneous removal of Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions from aqueous solutions via adsorption

Table 7. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Hg.

Ion	Zeolite type	Surface area of zeolite, m²/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Hg	CFA-Linde Type A	127.11	NA	0.4	50	2.5	10	10	Attari et al. [217]
Hg	CFA zeolite with AgNP	105	NA	6	7.5	2	10	100	Tauanov et al. [218]
Hg	K-type zeolite (FA48)	47.3	8.98	12	0.2	3	50	50	Kobayashi et al. [219]

on FAU-type zeolites synthesised from CFA. In this study, the selectivity sequence was in following order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+}$ with the adsorption capacity 12 mg/g for Co^{2+} ions.

Summarised results for Cobalt adsorption in single-ion system can be find in Table 8 and for mixed-ion systems in Table 10 in the Section 3.4.7.

3.4.6.4. Manganese. As mentioned previously, He et al. [195] studied the adsorption capacities of CFA zeolite in single and mixed-species aqueous solutions. In this study, the maximum adsorption capacities for Mn were established at 31 mg/g for a single species system and 15 mg/g for a five species system with an efficiency of 78 ± 0.7% for manganese in the Pb, Mn, Ni, Cu, Cd system.

Additionally, mixed-ions solutions were investigated by Qui et al. [208] and Nascimento et al. [209]. The study by Nascimento et al. [209] showed that the preferred order observed for adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+}, and Mn^{2+} using zeolites synthesised from Brazilian fly ash was $Pb > Cu > Mn \geq Zn$, with maximum adsorption capacity for Mn 60 mg/g. Qui et al. [208] used synthesised CFA zeolite for Cd, Cu, Mn, Ni, Pb and Zn adsorption. The results showed that the adsorption capacity followed the order of $Pb > Cu > Zn > Mn \approx Ni > Cd$. The maximum adsorption capacity for Mn ions was found 15 mg/g.

The results of Mn adsorption by CFA zeolites in single-ion systems are summarised in a Table 9

represented below. For mixed-ions systems, readers are referred to Table 10.

3.4.7. Mixed ion solutions

While single-ion systems give us important information on maximum adsorption capacity of selected zeolites for specific metal ions, mixed-ion systems are closer to a real-world scenario, where waste water typically contains various metal contaminants.

In Sections 3.4.1–3.4.6 research works examined CFA zeolites adsorption capacities for heavy metal ions in both single and mixed-species systems were described. For the readers' convenience, we divided studies on single and mixed-ion systems into individual Tables 1–10, where single-ion systems were presented in Tables 1–9 and mixed-ion combined in Table 10.

In order to better correlate the adsorption selectivity in mixed-ion systems, we summarised maximum adsorption capacities of different CFA zeolites in Table 10. For instance, it can be seen from researches by Visa et al. [194], He et al. [195], Joseph et al. [210], Qiu et al. [208], Nascimento et al. [209], Bai et al. [211] and Li et al. [212], that the adsorption capacity of different zeolites for Pb ions is greater than for other metal ions that are present in the system. At the same time, the maximum adsorption for Cu ions are greater than for Pb in studies by Wang et al. [200], Wang et al. [197] and Ji et al. [207].

Table 8. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Co.

Ion	Zeolite type	Surface area of zeolite, m²/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Co	CFA zeolite (Z-C1)	NA	NA	94	NA	NA	NA	NA	Lee et al. [220]

Table 9. Absolute adsorption capacities of different zeolites synthesised from CFA in single-ion solutions – Mn.

Ion	Zeolite type	Surface area of zeolite, m²/g	CEC, meq/g	Zeolite Adsorption Capacity, mg/g	Adsorbent Dosage, g/L	pH	Metal Ion Concentration, mg/L	Solution Volume, mL	References
Mn	CFA Zeolite	12.7	1.64	31	1	5	100	100	He et al. [195]

Table 10. Absolute adsorption capacities of different zeolites synthesised from CFA in mixed-ion systems.

Zeolite type	Surface area of zeolite, (m²/g)	CEC, (meq/g)	Metal ions in mixed-ion system	Adsorption Capacity (mg/g)	Adsorbent Dosage, (g/L)	pH	Metal Ion Concentration (mg/L)	Solution Volume (mL)	Reference
Magnetic zeolite P	29.5	NA	Cu	25	NA	NA	NA	50	Wang et al. [200]
			Pb	20					
Zeolite P	22.4	NA	Cu	30					
			Pb	28					
ZCET40	52.44	NA	Pb	88	4	6.6	0–1000	50	Visa et al. [194]
			Cd	27			0–600		
			Cu	21			0–250		
			Zn	8			0–260		
			Ni	6			0–250		
ZDs40	37.30	NA	Pb	98			0–1000		
			Cu	89			0–600		
			Cd	18			0–250		
			Zn	8			0–260		
			Ni	5			0–250		
4A	54.82	NA	Cu	50	5	3	50–300	100	Hui et al. [102]
			Cr	42					
			Zn	31					
			Co	14					
			Ni	9					
CFA Zeolite	12.7	1.64	Pb	45	1	5	100	100	He et al. [195]
			Cu	33					
			Cd	27					
			Ni	16					
			Mn	15					
NaP1	NA	NA	Cu	10	20	7	200	50	Wang et al. [197]
			Pb	1					
			Cd	0.3					
FAU-type zeolite (CFZ10−68)	432	NA	Pb	110	5	NA	100–500	20	Joseph et al. [210]
			Cu	58					
			Cd	53					
			Zn	37					
			Co	12					
Low calcium FA zeolite	3.26	3.06	Cu	198	10	6	100	100	Ji et al. [207]
			Pb	186					
			Zn	156					
			Cd	124					
High calcium FA zeolite	8.36	3.56	Cu	183					
			Pb	182					
			Zn	154					
			Cd	119					
Municipal solid waste incineration FA zeolite	40.12	0.498	Pb	50	12.5	3–4	500	20	Qiu et al. [208]
			Cu	28					
			Zn	20					
			Mn	15					
			Ni	14					
			Cd	11					
Zeolite A	NA	NA	Cu	38	5	3	300	100	Wang et al. [116]
			Zn	30					
Zeolite X	NA	NA	Cu	29					
			Zn	22					
CFA Zeolite	NA	NA	Pb	195	10	4–5	100–3000	50	Nascimento et al. [209]
			Cu	77					
			Mn	60					
			Zn	59					
Zeolite X	288.5	NA	Pb	112	1	7	100	50	Bai et al. [211]
			Cr	62					
			Cu	54					
			Zn	45					
			Cd	38					
CFA Composite Zeolite	96.5	NA	Pb	122	0.5	4.5	100 ± 10	100	Li et al. [212]
			Cr	71					
			Cu	34					
			Zn	28					
			Cd	10					
			Ni	5					

The reasons for a certain selectivity order of metal ions uptake, however, have not yet been given a definitive explanation in the literature. Therefore, more research in this field may help us comprehend the relationship between synthesised zeolite and other experimental parameters and metals selectivity sequence.

4. Conclusions

Natural zeolites are a well-known group of minerals with good mechanical and thermal properties and high sorption capacity. They are widely used in the field of heterogeneous catalysis and have many other industrial applications. However, due to the limited variety of natural zeolite microstructures and surface chemistry, synthetic zeolites often outperform natural zeolites. The sorption capacity of synthetic zeolites using various synthesis methods with designed chemical properties and pore size has been the subject of many studies. CFA is the waste product of one of the most widely used electricity production processes worldwide, so productively utilising CFA can alleviate environmental impacts. Furthermore, zeolites synthesised from CFA could be an alternative to other, more expensive adsorbents.

Due to the superior adsorption capacities achieved by synthetic zeolites, they are a promising material for water treatment applications, including heavy metal remediation. Unique ion exchange and adsorption properties, high porosity, and thermal stability make zeolites suitable for water treatment processes. Water is an essential resource, pollution of which is one of the leading causes of water shortages worldwide. The diversion of a waste stream such as a CFA to an ecologically beneficial process is likely to be important in the coming years. There are numerous researchers investigating CFA-synthesised zeolite-based water remediation processes. However, in most studies, researchers investigated zeolite adsorption capacity in a batch process. While it shows the ability of the investigated zeolites to be efficiently applied water remediation, investigations of continuous processes would be of significant interest and value because to the industrial wastewater streams require a continuous system.

Zeolites synthesised from CFA have been demonstrated as being effective heavy metal adsorbents for heavy metal ions both from single and multi-cation solutions. While these zeolites' carrying capacity is comparable or better than commercial products, care should be taken to tailor the adsorbent to the ions that require remediation. As has been detailed in this overview, the type of synthesised zeolite plays a significant role in the adsorption process both in single and mixed-ion solutions. Furthermore, in mixed ion solutions, the selectivity order is affected by zeolite choice, a feature that could be leveraged to mitigate the effects of competition in such systems. However, currently, there seems to be no explicit reason in the literature as to why specific zeolites and their characteristics result in a specific selectivity order. Consequently, further research could provide a better explanation for the relationship between zeolite choice and the selectivity series. Such a model could then be utilised in the rational design of synthetic zeolites for specific remediation targets.

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