

Practical Application of Zeolites as Adsorbent

Subjects: Water Resources

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Zeolites are crystalline micro- and mesoporous materials widely used as catalysts and sorbents. Zeolites are commonly used in separation processes in, e.g., the petrochemical and pharmaceutical industries as they can be made fairly specific to the target molecules, and since the main mechanisms behind the separation process (molecular sieving, electrostatic interaction, and polarization) are always reversible, zeolites are believed (under ideal situations) to be able to undergo a virtually unlimited number of adsorption–desorption cycles. This is important from a cost-efficiency perspective too, as the high initial costs can be compensated by the longer life, assured by excellent stability and ease of regeneration.

Keywords: municipal solid waste (MSW) ; fly ash (FA) ; zeolites ; adsorbent ; magnetic zeolites ; powdered zeolites

1. Introduction

There is an increasing interest in using incineration to dispose of municipal solid waste (MSW) due to the large reduction in weight (up to 70%) and volume (up to 90%), the concomitant recovery of energy and heat, and the destruction of most of the hazardous organic contaminants and pathogens. The globally generated amount of MSW increased significantly from 1.3 billion tons per annum in 2012 to 2.1 billion tons in 2018 ^[1], which is expected to increase further to 3.4 billion tons per year by 2050 ^[2]. Upon incineration, three main residues are produced: bottom ash, fly ash (FA), and air pollution control (APC) residues. Approximately 250–300 kg of bottom ash, 25–30 kg of fly ash, and APC residues are generated for each ton of MSW incinerated ^[3]. The bottom ash residue is utilized in many applications, particularly in building and construction work. The FA residue, however, is generally regarded as toxic waste due to its high content of heavy metals, salts, and organic micropollutants such as dioxins and furans ^[4] owing to the volatilization and condensation of different elements during the incineration. Therefore, nearly all MSW incineration FA (MSW-FA) is stabilized/solidified and deposited as toxic waste in landfills, and due to their enormous volumes, taking up valuable space. However, a shift in focus from environmental impacts to resource recovery has identified the potential value of embedded salts and metals in the MSW-FA, and some progress has been made in recovering these resources ^{[5][6][7]}.

The principal components of FA are CaO, SiO₂, Al₂O₃, and Fe₂O₃, resembling the main components of volcanic material, a precursor of natural zeolites. Zeolites are crystalline micro- and mesoporous materials widely used as catalysts and sorbents ^[8]. However, most of the zeolites that are used today are synthesized since natural zeolites vary too much in mineralogical and chemical composition, crystal structure, and pore sizes, both between and within the mineral deposits they are extracted from, to be used for applications that require zeolites with specific and predictable properties ^[9]. Zeolites are primarily synthesized from pure silica (SiO₂) and alumina (Al₂O₃), though the search for and use of alternative economical and abundant sources has increased in the last decades ^[10]. Due to its low cost, availability, abundance, and resemblance to volcanic material, it is relatively common to synthesize zeolite from coal-derived FA ^[11]. MSW-FA usually contains much less silica and alumina than coal-derived FA ^{[10][11]}. Moreover, the often-high levels of leachable toxic compounds in this type of FA need to be reduced ^[12].

Zeolites, depending on their chemical composition and pore structures as well as the operating conditions, can be used as sorbents for the removal of mono-, di-, and trivalent cations such as ammonium (NH₄⁺) and heavy metals (Pb²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Cr³⁺, and Ni²⁺) from industrial and municipal wastewaters ^[13]. And, by subsequent desorption and refinement, if needed, these adsorbates can be recovered for further downstream applications ^{[11][14]}. Furthermore, certain surface modifications of the zeolites can also be used as sorbents to remove anions such as phosphate (PO₄³⁻), nitrate (NO₃⁻), and arsenate (H₂AsO₄⁻, HAsO₄²⁻, AsO₄³⁻). However, the recovery of the adsorbates and the regeneration of the SMZ may be low.

The need to drastically improve the recovery of phosphorous from available sources due to the reduced availability of non-renewable phosphate rock is well known. Crop residues, food waste, manure, and human excreta are such sources, and multiple methods and strategies are currently under development to facilitate cost-effective means to harvest phosphorous from these, including from domestic wastewater ^[15], primarily for use in agriculture ^[16]. Nitrogen, on the

other hand, is not a scarce resource, but the industrial production of mineral fertilizers consumes extensive amounts of energy and natural gas as feedstock for the hydrogen gas in the production of ammonia. Jensen and Kongshaug (2003) [17] estimated that fertilizer production accounted for approximately 1.2% of global energy consumption, of which about 93% was consumed by nitrogen-based fertilizers. Moreover, extensive nitrogen removal up to 85% at wastewater treatment plants (WWTP), as proposed by the European Commission in the revised version of the urban waste water treatment directive [18], implies a huge increase in investments, operating costs, and energy consumption to comply with the more stringent discharge requirements for nitrogen while losing approximately 60% of the nitrogen as nitrogen gas.

When the zeolite is used as an adsorbent in practical applications, it is crucial to make sure that its adsorption characteristics (i.e., rate, kinetic, and capacity) are utilized to the fullest and that it will be a rather simple task to separate the zeolite from the water. Since synthesized zeolites are typically powders with particles in the nm-to- μm size range, they will be very easily dispersed in water. Their small size is one of their main strengths as adsorbents, as their surface-to-volume ratio is very large. Hence, it will be beneficial if this can be retained in practical applications.

2. Production and Use of Shaped and Structured Zeolites

However, in practice, the zeolites are usually transformed into larger aggregates prior to industrial use, either by granulation into beads or pellets (i.e., structured zeolites) or by extrusion in the shapes of, e.g., cylinders (monoliths) (i.e., shaped zeolites) [19][20]. This is done to improve its mechanical and physical properties and to prevent or minimize pressure drop, material loss, and erosion of equipment when applied to, e.g., fixed-bed or expanded-bed filtration units [19]. In most cases, this includes the addition of water and other inorganic (e.g., clay, silica, or alumina) and/or organic binders that fill the gaps between the zeolite crystals and hold them together in the final material. Other additives may also be added to provide appropriate plasticity or porosity [20]. After shaping, the material is usually dried and calcined to remove water and labile components, and to achieve the final mechanical properties, residual binders typically constitute 5–30% of the final material [19][21]. However, this type of shaping or structuring can greatly affect the adsorption capacity and kinetics of the zeolite [20][22]. The introduction of different types of hierarchical aluminas (ordered and disordered mesoporous and macroporous structures) to improve the porosities in the binders has been suggested; see Bingre et al. (2018) [20] for a review.

3. Physical Separation of Powdered Zeolites—Magnetic Zeolites

Powdered zeolites may, as is frequently done with powdered activated carbon (PAC), be applied, e.g., directly to the aeration basin of an activated-sludge treatment process and to physical-chemical treatment processes in conjunction with chemicals used for the precipitation of specific constituents [23]. In both of these examples, the existing treatment train includes a unit (typically a sedimentation tank or rapid sand filter) to separate the sludge generated by the process, and the powdered zeolites (or PAC) will normally also be collected with the sludge. Otal et al. (2013) [24] added 1 g/L of a NaP1 zeolite synthesized from coal FA to a poorly settleable activated sludge, significantly improving the settling performance of the sludge and removing 30% of the nitrogen (13.7 mg NH_4/g). It may also be applied to the effluent from a biological treatment process in a contacting basin. After a certain amount of time for contact, the zeolite particles (or PAC) are allowed to settle to the bottom of the tank, and the treated water is then removed from the tank [23]. In practice, to accelerate the settling rate of the powdered zeolites (or carbon), a flocculant (e.g., a polyelectrolyte) is added to aggregate the fine-grained particles. The flocculant must be removed (e.g., by calcination) if the powdered zeolites should be reused. To avoid using additional chemicals, filtration through a rapid sand filter may be used. However, the typical nm- μm size range of powdered zeolites may imply that it will be challenging to get sufficient separation by traditional sand filtration without the aid of additional sludge or flocculant, as these typically have a cut-off range of 2–10 μm [23].

The application of magnetic zeolites could, however, be a solution to this challenge [25]. By incorporating magnetic nanoparticles in the zeolite crystals, the composite will respond to an external magnetic field by forming aggregates (magnetic separation), which will settle much faster. When the magnetic field is removed, the aggregation will stop [25]. Hence, the magnetized zeolitic particle will replace the need for a flocculant and facilitate its reuse. Magnetic separation offers a significant improvement in operation efficiency and reduced costs [25].

It is important that the modification be strong enough to provide the zeolite particles with sufficient magnetic properties without altering the structure or adsorption properties of the zeolite [25]. Typical materials used to produce magnetic zeolites include metal nanoparticles (Fe, Co, Ni, etc.), ferrites (MFe_2O_4 ; $\text{M} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , etc.), alloys (CoPt_5 , FePt , etc.), and iron oxides (Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$) [26]. Magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are most commonly used as these are relatively cheap materials, biocompatible, and environmentally safe [25][27]. However, the clear drawbacks of using Fe_3O_4 as a magnetic nanoparticle in the composite are that it tends to both agglomerate and react rapidly [28]. The

often-preferred method to prepare iron oxide nanoparticles is by co-precipitation of Fe^{3+} and Fe^{2+} salts, as it is regarded as a facile and green synthesis method [25].

It is not the intention of this review to summarize all the different methods that have been used to prepare magnetic zeolites (see, e.g., Loiola et al. 2022 [25], Phouthavong et al. 2022) [29]; however, it should be noted that the embedding of magnetic nanoparticles in or on zeolites can be done both during and after the synthesis of zeolites.

Based on 25 years of published works, Loiola et al. (2022) [25] suggested that the numerous composite compounds that had been developed could be classified in five groups based on the position of the magnetic particles in the zeolite crystals: magnetic particles are encapsulated by the zeolitic structure (Type I), the zeolite surface is impregnated or decorated with magnetic nanoparticles (Type II), each magnetic particle is covered with zeolite layers (Type III), nanoagglomerates of small (<100 nm) particles of both zeolites and magnetic compounds (Type IV), and tri-modal composites in which the magnetic zeolite composite is dispersed in a polymer matrix. According to Loiola et al. (2022) [25], type II composites are currently the most relevant and common magnetic zeolites found in this literature, mainly for being easily obtained and usually for not having a negative impact when the nanoparticles are embedded. However, type V composites are the most promising ones in the long term since they solve problems related to agglomeration of constituents, oxidation, and leaching [25]. They are also more mechanically, chemically, and electrically stable [25].

However, improvements in magnetic adsorbent synthesis are still needed to make it more effective, give more uniform magnetic distribution, and break the barrier of the laboratory with scalable processes for their mass production [29].

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